

## TRANSMITTAL LETTER TO THE UNITED STATES

DESIGNATED/ELECTED OFFICE (DO/EO/US)

CONCERNING A FILING UNDER 35 U.S.C. 371

A32851-PCT-USA

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

09/462387

INTERNATIONAL APPLICATION NO.  
PCT/EP98/03917INTERNATIONAL FILING DATE  
26 June 1998 (26.06.98)PRIORITY DATE CLAIMED  
09 July 1997 (09.07.97)

## TITLE OF INVENTION

SILICA-CONTAINING RUBBER COMPOSITION VULCANIZABLE WITH SULFUR

## APPLICANT(S) FOR DO/EO/US

DANIEL, Marc and LABAUZE, Gerard

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
  - a. ☒ is transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☐ has been transmitted by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ A copy of the International Search Report (PCT/ISA/210).
8. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
  - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☐ have been transmitted by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☒ have not been made and will not be made.
9. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
10. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
11. ☒ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).

## Items 13 to 18 below concern document(s) or information included:

13. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☒ A **FIRST** preliminary amendment.
16. ☒ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☒ Certificate of Mailing by Express Mail
19. ☒ Other items or information:

A substitute Abstract; Forms PCT/RO/101 and 105; Forms PCT/IPEA/401 and 402; Form PCT/IB/304, a postcard, refs. cited in the IDS, and a check in the amount of \$970.00.

Express Mail No. EJ339569224US

Date of Deposit: 06 January 2000

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 09/1462387	INTERNATIONAL APPLICATION NO. . PCT/EP98/03917	ATTORNEY'S DOCKET NUMBER A32851-PCT USA
--	---	--

20. The following fees are submitted:.

**BASIC NATIONAL FEE ( 37 CFR 1.492 (a) (1) - (5) ) :**

- |   |                 |
|---|-----------------|
| <input type="checkbox"/> Search Report has been prepared by the EPO or JPO .....  | <b>\$840.00</b> |
| <input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1.482)<br>.....  | <b>\$670.00</b> |
| <input type="checkbox"/> No international preliminary examination fee paid to USPTO (37 CFR 1.482)<br>but international search fee paid to USPTO (37 CFR 1.445(a)(2)) .....   | <b>\$760.00</b> |
| <input checked="" type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor<br>international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... | <b>\$970.00</b> |
| <input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1.482)<br>and all claims satisfied provisions of PCT Article 33(2)-(4) .....         | <b>\$96.00</b>  |

**ENTER APPROPRIATE BASIC FEE AMOUNT =****CALCULATIONS** PTO USE ONLY

**\$970.00**

Surcharge of **\$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).

**\$0.00**

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	
Total claims	12 - 20 =	0	x \$18.00	\$0.00
Independent claims	1 - 3 =	0	x \$78.00	\$0.00
Multiple Dependent Claims (check if applicable).			<input type="checkbox"/>	\$0.00

### TOTAL OF ABOVE CALCULATIONS

**\$970.00**

Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) (check if applicable).

**\$0.00**

**SUBTOTAL =**

**\$970.00**

Processing fee of **\$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (f)).

**\$0.00**

**TOTAL NATIONAL FEE**

**\$970.00**

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) **(check if applicable)**.

**\$0.00**

**TOTAL FEES ENCLOSED**

**\$970.00**

**Amount to be:**

§

**charged**

\$

- ☒ A check in the amount of **\$970.00** to cover the above fees is enclosed.
- ☐ Please charge my Deposit Account No. \_\_\_\_\_ in the amount of \_\_\_\_\_ to cover the above fees.  
A duplicate copy of this sheet is enclosed.
- ☒ The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. **02-4377** A duplicate copy of this sheet is enclosed.

**NOTE:** Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

**SEND ALL CORRESPONDENCE TO:**

**Rochelle K. Seide, Ph.D.**  
**BAKER BOTTS LLP**  
**30 Rockefeller Plaza**  
**New York, NY 10112-0228**

SIGNATURE

**Rochelle K. Seide**

NAME \_\_\_\_\_

**32,300**

REGISTRATION NUMBER

**06 January 2000**

DATE \_\_\_\_\_

09/462387

FILE NO. A32851-PCT-USA-070338.0556

428 Rec'd PCT/PTO 06 JAN 2000

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant : Daniel, et al.  
Serial No. : Examiner:  
Filed : July 9, 1997 Group Art Unit:  
For : SILICA-CONTAINING RUBBER COMPOSITION  
VULCANIZABLE WITH SULFUR

**PRELIMINARY AMENDMENT**

Assistant Commissioner for Patents  
**Box PCT**  
Washington, D.C. 20231

Sir:

Prior to examination of the present application, please make the following  
amendments.

**IN THE SPECIFICATION:**

Please substitute the attached specification (42 pages) for the original PCT  
specification (and translation).

**IN THE CLAIMS:**

Please cancel original Claims 1-12 and substitute therefor new Claims 13-27 as

005749 2829450

follows:

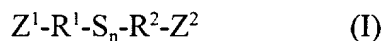
13. (New) Rubber composition vulcanizable with sulfur, characterized in that it comprises

a) at least one polymer selected from the group consisting of diene polymers, olefin/monomeric diene copolymers and halogenated isoolefin/para-alkylstyrene copolymers;

b) silica as filler;

c) at least one agent promoting linking between the silica and the polymer,

said agent having the formula

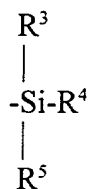


wherein

n is an integer between 2 and 8,

R<sup>1</sup> and R<sup>2</sup>, which may be the same or different, are each selected from among substituted or unsubstituted alkylene groups having 1 to 18 carbon atoms and of substituted or unsubstituted arylene groups having 6 to 12 carbon atoms,

Z<sup>1</sup> and Z<sup>2</sup>, which may be the same or different, each represents a group



wherein R<sup>3</sup>, R<sup>4</sup> and R<sup>5</sup>, which may be the same or different, are each selected from among alkyl groups having 1 to 4 carbon atoms, phenyl groups, alkoxy groups having 1

to 8 carbon atoms, and cycloalkoxy groups having 5 to 8 carbon atoms, with the proviso that at least one of  $R^3$ ,  $R^4$  and  $R^5$  is an alkoxy or cycloalkoxy; and

d) at least one guanidine substituted by at least two groups, which may be the same or different, and each selected from among alkyl, aryl or aralkyl groups;

wherein the composition satisfies at least one of the following features (i) and/or (ii):

- (i) the composition comprises at least one diene polymer which has at least one amino terminal group of an aliphatic or cycloaliphatic amine which is bonded thereto at the end of the chain, the polymer then being devoid of alkoxysilane and silanol group; and
- (ii) the composition comprises at least one free aliphatic or cycloaliphatic amine.

14.(New) Composition according to Claim 13, wherein the filler is silica.

15. (New) Composition according to Claim 14 wherein the filler comprises at least 40% by weight of silica.

16. (New) Composition according to Claim 13 wherein in the linking agent of formula (I),  $n$  is greater than 2, or if there are several such agents, at least 80% of  $n$  is greater than 2 for the total of these agents.

1           17. (New) Composition according to Claim 13 wherein the agent of formula (I) or  
2 mixture of such agents comprises at least 4% by weight calculated on the weight of silica  
3 or mixture comprising silica used as filler.

1           18. (New) Composition according to Claim 13 wherein the guanidine or mixture  
2 of guanidines comprises 0.5 to 4% by weight calculated on the weight of silica or mixture  
3 of silicas as filler.

1           19. (New) Composition according to Claim 18 wherein the guanidine or mixture  
2 of guanidines comprises 1 to 3% by weight of the filler.  
3

1           20. (New) Composition according to Claim 13, wherein the free aliphatic or  
2 cycloaliphatic amine, or mixture of free aliphatic or cycloaliphatic amines, comprises 0.5  
3 to 4% by weight calculated on the weight of silica or mixtures of silicas as filler.

4           21. (New) Composition according to Claim 20 wherein the aliphatic or  
5 cycloaliphatic amine comprises 1 to 3% by weight of filler.

1           22. (New) Composition according to Claim 13, comprising at least one free  
2 aliphatic or cycloaliphatic amine homogeneously dispersed in the composition.

## PATENT

1           23. (New) Composition according to Claim 22, wherein the polymer is prepared  
2           in solution and that the aliphatic or cycloaliphatic amine is introduced into this solution  
3           after stopping the polymerization and before stripping of the solvent.

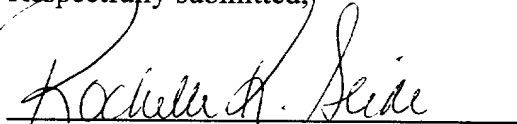
4           24. (New) Tire tread comprising at least one composition according to Claim 13.

1           25. (New) Tread obtained by vulcanization of the tread according to Claim 24.

26. (New) Tire casing comprising at least one composition according to Claim 13.

27. (New) Tire casing obtained by vulcanizing the tire casing according to Claim  
26.

Respectfully submitted,



Rochelle K. Seide

Patent Office Reg. No. 32,300

Attorneys for Applicants

(212) 408-2626

Enclosures

(1) Substitute Specification (42 pages)

(2) Abstract

**SILICA-CONTAINING RUBBER COMPOSITION  
VULCANIZABLE WITH SULFUR**

The present invention relates to elastomer compositions comprising silica as reinforcing filler, said compositions having improved hysteretic properties in the vulcanized state.

Since economizing on fuel and protection of the environment have become priorities, it is desirable to produce mixtures having the lowest possible hysteresis, in order to be able to use them as semi-finished products which enter into the make-up of tire casings, semi-finished products such as undercoats, binding gums between rubbers of different types, or for calendering metallic or textile reinforcements, sidewall gums or treads, and to obtain tires with improved properties, said tires having a reduced resistance to rolling in particular.

To achieve this objective, numerous solutions have been proposed consisting, in particular, in modifying the nature of the diene polymers and copolymers at the end of polymerization by means of coupling agents, starring agents or functionalizing agents. The great majority of these solutions are essentially concentrated on the use of polymers modified with carbon black as reinforcing filler, with a view to obtaining a good interaction between the modified polymer and the carbon black, since the use of white reinforcing agents, notably silica, has proved inappropriate owing to the low value of



some of its properties, and, as a result, of certain properties of the tires using these compositions.

As an illustrative example from the prior art, mention may be made of U.S. Patent 4,677,165, which describes the reaction of living diene polymers functionalized by means of a benzophenone derivative to obtain polymers having improved properties in compositions containing carbon black as reinforcing filler.

EP-A-0,451,604 describes, as functionalizing agent, a compound having an amino function and which permits an improved interaction between the modified polymers and carbon black. With the same objective, U.S. Patent 4,647,625 describes the functionalization of elastomers by reaction of a living polymer with N-methylpyrrolidine. EP-A-0,590,491 and EP-A-0,593,049 describe polymers having a tertiary amino function at the end of the chain and also permitting better interaction with carbon black.

Certain solutions have also been proposed concerning the use of silica as reinforcing filler in the compositions designed to constitute treads of tires. Proposed for this purpose have been functionalized polymers comprising alkoxysilane functions at the end of the polymer chains, as described in

EP-A-0,299,074 and EP-A-0,447,066. It is only these functionalized polymers that have been described in the prior art as being effective in reducing the hysteresis and improving the resistance to abrasion, but the industrial manufacture of these polymers poses problems due to macrostructure development during the recovery stages such as stripping or drying. To attempt to solve these problems, it has been proposed to use polymers functionalized with non-hydrolyzable alkoxysilane functions, as described in U.S. Patent 5,066,721, but their effectiveness in a mixture with silica is reduced. The

preparation of diene polymers having an amino function is known to persons skilled in the art, e.g. from U.S. Patent 4,894,409, which describes the preparation of polymers functionalized with aromatic amines. The polymers having an amine function are not very effective when used with silica, as mentioned in EP-A-0,661.298.

This interest in silica-reinforced compositions was revived with the publication of EP-A-0,501,227 which discloses a rubber composition vulcanizable with sulfur, obtained by thermomechanical working of a copolymer of a conjugated diene and a vinylaromatic compound, prepared by solution polymerization, with 30 to 150 parts by weight per 100 parts by weight of elastomer of a particular precipitated silica, which represents an excellent compromise between several contradictory properties, and which for the first time permits the commercialization of tires possessing a silica-filled tread showing the excellent compromise that is required.

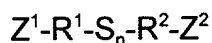
The present invention relates to a new rubber composition containing silica or a mixture of silica and carbon black as reinforcing filler, said composition having satisfactory properties when used in the crude state and improved properties in the vulcanized state, particularly an excellent hysteresis and excellent reinforcement.

The invention also relates to treads of tire casings having at least one composition in accordance with the invention, as well as to treads obtained by vulcanization of these treads.

The invention also relates to casings of tires comprising at least one composition according to the invention, as well as to tire casings obtained by vulcanization of these casings, at least one composition of the invention being used e.g. in the tread.

The rubber composition vulcanizable with sulfur, according to the invention, is characterized in that it comprises:

- a) at least one polymer selected from the group consisting of diene polymers, olefin/monomeric diene copolymers and halogenated isoolefin/para-alkylstyrene copolymers;
- b) silica as filler;
- c) at least one agent promoting binding between silica and polymer, said agent having the formula (I)

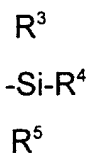


wherein

n is an integer between 2 and 8,

R<sup>1</sup> and R<sup>2</sup>, which may be the same or different, are each selected from the collective comprising substituted or unsubstituted alkylene groups having a total of 1 to 18 carbon atoms and substituted or unsubstituted arylene groups having a total of 6 to 12 carbon atoms,

Z<sup>1</sup> and Z<sup>2</sup>, which may be the same or different, each represents a group



where R<sup>3</sup>, R<sup>4</sup> and R<sup>5</sup>, which may be the same or different, are each selected from the collective comprising alkyl groups having 1 to 4 carbon atoms, phenyl groups, alkoxy groups having 1 to 8 carbon atoms, and cycloalkoxy groups having 5 to 8 carbon atoms, on condition that at least one of R<sup>3</sup>, R<sup>4</sup> and R<sup>5</sup> is an alkoxy or cycloalkoxy;

d) at least one guanidine substituted by at least two groups which may be the same or different and selected from the collective comprising alkyl, aryl or aralkyl groups;

and in that it has at least one of the following characteristics:

- It comprises at least one diene polymer which has at least one terminal amino group of an aliphatic or cycloaliphatic amine which is bonded thereto at the end of the chain, the polymer then being devoid of alkoxysilane and silanol group;

- The composition comprises at least one free aliphatic or cycloaliphatic amine.

In what follows, the term "polymer" covers both homopolymers and copolymers; the term "copolymer" referring to polymers obtained from two or more than two monomers, e.g. terpolymers.

Understood by a diene polymer is any homopolymer obtained by polymer-ization of a conjugated diene monomer having 4 to 12 carbon atoms, any copolymer obtained by copolymerization of one or more conjugated diene with each other or with one or more vinylaromatic compounds having 8 to 20 carbon atoms. As conjugated diene, mention may be made of e.g. 1,3-butadiene,

2-methyl-1,3-butadiene, 2,3-di(C<sub>1</sub>-C<sub>5</sub>-alkyl)-1,3-butadiene such as, e.g., 2,3-dimethyl-1,3-butadiene, 2,3-diethyl-1,3-butadiene, 2-methyl-3-ethyl-1,3-butadiene, 2-methyl-3-isopropyl-1,3-butadiene, phenyl-1,3-butadiene, an aryl-1,3-butadiene, 1,3-pentadiene, and 2,4-hexadiene.

Suitable as vinylaromatic compounds are, in particular, styrene, ortho-, meta- and paramethylstyrene, the commercial "vinyl-toluene" mixture, p-tert.-butylstyrene, the

methoxystyrenes, chlorostyrenes, vinylmesitylene, divinylbenzene, and vinylnaphthalene.

The copolymers may contain e.g. between 99% and 20% by weight of diene units and from 1% to 80% by weight of vinylaromatic units. The polymers may have any microstructure, which is a function of the polymerization conditions used, notably of the presence or absence of a modifying agent and/or random-izing agent and of the amounts of modifying and/or randomizing agent used.

Polybutadienes are preferred, particularly those having a 1,2-units content of between 1% and 80%, as well as polyisoprenes, copolymers of butadiene and styrene and, in particular, those having a styrene content of between 5 and 50% by weight, and more particularly between 20% and 40% by weight, a 1,2-bond content of the butadiene part of between 4% and 65%, and a trans-1,4 bond content of between 30% and 80%. Suitable in the case of butadiene-styrene-isoprene copolymers are those having a styrene content of between 5 and 50% by weight, and more particularly between 10% and 40%, an isoprene content of between 15% and 60% by weight, more particularly between 20% and 50% by weight, a butadiene content of between 5% and 50% by weight and more particularly between 20% and 40% by weight, a 1,2-units content of the butadiene part of between 4% and 85%, a trans-1,4 units content of the butadiene part of between 6% and 80%, a 1,2-units content plus 3,4-units content of the isoprene part of between 5% and 70%, and a trans-1,4-units content of the isoprene part of between 10% and 50%.

When the diene polymer has an amino terminal group, it is then devoid of alkoxy silane group and silanol group and may be a homopolymer or copolymer

obtained from the above-mentioned monomers, and said polymer can be obtained by initiation or functionalization.

In the case where the terminal amino group is introduced by initiation, the polymerization is advantageously carried out with an initiator of the lithium amide type, as described in the literature, e.g. in the work of T.C. Cheng, "Anionic Polymerization," published by the American Chemical Society, Washington, p. 513, 1981, whose content is incorporated herein. This lithium amide, of formula



wherein  $R_1$  and  $R_2$ , independently of one another, are an alkyl group, or together form a cycloalkyl, the number of carbon atoms of the compound formed by  $R_1$  and  $R_2$  preferably being 2 to 15.

As a preferred example,  $R_1$  and  $R_2$  may each be an ethyl or butyl radical, or together form a cycloalkyl radical having 4 to 6 carbon atoms.

When necessary, the initiator of formula (II) is prepared in the presence of a polar agent such as tetrahydrofuran, by reacting the corresponding amine  $R_1-NH-R_2$  such as hexamethyleneimine, with an alkyl lithium, such as n-butyllithium.

In the case where the amino end group is introduced by functionalization at the end of polymerization, the functionalization procedures described in e.g. EP-A-451,604, U.S. Patent 4,647,625 or in "Synthesis of polymers with amino end groups. Part 3. Reactions of anionic living polymers with  $\alpha$ -halo- $\omega$ -aminoalkanes with a protected

amino functionality,” (Kenji Ueda et al., Macromolecules 1990, 23, pages 939-945) may be used.

The polymerization may be carried out by a continuous or a discontinuous process. The polymerization is generally done at a temperature between 20°C and 120°C, preferably between 30°C and 90°C.

The olefin/diene copolymers can be, notably, EPDM's (ethylene-propylene-diene monomer) such as ethylene-propylene-1,4-hexadiene copolymers, ethylene-propylene-ethylidenenorbornene copolymers, ethylene-propylene-dicyclopentadiene copolymers, butyl rubbers, particularly isobutylene-halogenated isoprene copolymers, as the case may be. The isoolefin/ halogenated para-alkylstyrene copolymers can, e.g. be the isobutylene-/ halogenated para-methylstyrene rubber marketed by Exxon under the trade name EXXPRO.

The polymers may be e.g. block polymers, statistical polymers, sequenced polymers, microsequenced polymers, and be prepared by dispersion polymerization, solution polymerization, bulk polymerization, or in a gaseous phase.

The composition according to the invention may comprise a mixture of two or more polymers defined above.

The free aliphatic or cycloaliphatic amine may be a primary, secondary or tertiary amine. By way of nonlimitative examples, mention may be made, e.g. of the following amines: butyl, dibutyl, tributylamines, pentyl, dipentyl, tripentylamines, hexyl, dihexyl, trihexylamines, cyclohexyl, dicyclohexyl, tricyclohexyl amines, benzyl, dibenzyl, tribenzylamines, octyl, dioctyl, trioctylamines, decyl, didecylamines, dodecyl,

didodecylamines, pyrrolidine and alkyl pyrrolidines, piperidine and alkylpiperidines, hexamethyleneimine and alkylhexamethyleneimines, said amines may be suitable for use alone or in a mixture with one another.

Preferably, the free amine content or the mixture of free amines ranges from 0.5 to 4% by weight calculated on the total weight of silicas, said content advantageously being between 1 and 3% by weight.

The substituted guanidine may e.g. be triphenylguanidine, diphenylguanidine, or di-o-tolylguanidine. The composition may comprise a mixture of two or more substituted guanidines.

The content of substituted guanidine or mixture of substituted guanidines is 0.5 to 4% by weight calculated on the silica or total of silicas, said content advantageously being 1 to 3% by weight.

The silica used as filler may be any silica known to persons skilled in the art having a BET surface of less than or equal to 450 m<sup>2</sup>/g, a specific surface area CTAB or less than or equal to 450 m<sup>2</sup>/g, even though this improvement is more pronounced with a highly dispersible precipitated silica. Understood by the term "highly dispersible silica" is any silica capable of deagglomeration and dispersion in a very large amount of polymeric matrix, observable on fine sections by electron microscopy or optical microscopy. Nonlimitative examples of such preferred, highly dispersible silicas are those obtained according to the processes described in EP-A-0,157,703 and EP-A-0,520,862, or the Zeosil silica 1165 MP of Rhône-Poulenc, the Perksasil silica KS 430 of Akzo, silica Hi-Sil 2000 of PPG, silicas Zeopol 8741 and Zeopol 8745 of Huber Co. According to the invention, the beneficial effect is obtained regardless of the physical



state in which the silica is present, i.e whether it is in powder form, micropearl form, granulated form, spherical form, and regardless of what the specific surface area of the silica is. To be sure, it is also possible to use blends of different silicas and use other white fillers, such as chalk, kaolin or alumina.

In combination with silica, it is possible, if necessary, to use carbon black in the reinforcing filler, notably all carbon blacks that are commercially available or conventionally used in tires, particularly in treads.

The filler consists essentially of one or more silicas or it contains at least 40% by weight – and advantageously at least 50% by weight – of a silica or mixture of silicas.

The reinforcing filler, which may thus comprise silica without carbon black or both silica and carbon black, is present in the composition in an amount which may range e.g. from 30 to 100 parts by weight of the polymer or ensemble of polymers.

By way of examples of an agent of formula (I) which promotes linking between silica or combination of silicas and the diene polymer or ensemble of diene polymers, mention may be made of the 2,2'-bis(trimethoxysilylethyl) polysulfides, the 3,3'-bis(trimethoxysilylpropyl) polysulfides, the 3,3'-bis (triethoxysilylpropyl) polysulfides, the 2,2'-bis(triethoxysilylpropyl) polysulfides, the 2,2'-bis(tripropoxysilylethyl) polysulfides, the 2,2'-bis(tri-sec.-butoxysilylethyl) polysulfides, the 3,3'-bis(tri-tert.-butoxyethyl) polysulfides, the 3,3'-bis (triethoxysilylethyltolylene) polysulfides, the 3,3'-bis(trimethoxy-silylethyltolylene) polysulfides, the 3,3'-bis(triisopropoxypropyl) polysulfides, the 3,3'-bis (trioctoxypropyl) polysulfides, the 2,2'-bis(2'-ethylhexoxysilylethyl) polysulfides, the 2,2'-bis(dimethoxy-ethoxysilylethyl) polysulfides, the 3,3'-bis(methoxyethoxypropoxysilylpropyl) polysulfides, the 3,3'-

bis(methoxydimethylsilylpropyl) polysulfides, the 3,3'-bis(cyclohexoxydimethylsilylpropyl) polysulfides, the 4,4'-bis(trimethoxy-silylbutyl) polysulfides, the 3,3'-bis(trimethoxysilyl-3-methylpropyl) polysulfides, the 3,3'-bis(tripropoxysilyl-3-methylpropyl) polysulfides, the 3,3'-bis(trimethoxymethylsilyl-3-ethylpropyl) polysulfides, the 3,3'-bis(trimethoxy-silyl-2-methylpropyl) polysulfides, the 3,3'-bis(dimethoxyphenylsilyl-2-methylpropyl) polysulfides, the 3,3'-bis(trimethoxysilylcyclohexyl) polysulfides, the 12, 12'-bis(trimethoxysilyldodecyl) polysulfides, the 12, 12'-bis(triethoxysilyl-dodecyl) polysulfides, the 18, 18'-bis(trimethoxysilyloctadecyl) polysulfides, the 18, 18'-bis(methoxydimethylsilyloctadecyl) polysulfides, the 2,2'-bis(trimethoxysilyl-2-methylethyl) polysulfides, the 2,2'-bis(triethoxysilyl-2-methylethyl) polysulfides, the 2,2'-bis(tripropoxysilyl-2-methylethyl) polysulfides, and the 2,2'-bis(trioctoxysilyl-2-methylethyl) polysulfides. Such a linking agent is e.g. that sold by Degussa under the trade designation Si69 whose average formula is bis(3-triethoxysilylorioyl) tetrasulfide. These polysulfides can be used alone or in a mixture with each other.

By preference, n in the linking agent of formula (I) is greater than 2, or if there are several such agents, at least 80% of n is greater than 2 for the total of these compounds.

The content of the agent of formula (I) or mixture of such agents is preferably at least 4% of the weight of silica or of the mixture of silicas used as filler.

The compositions according to the invention can also contain other constituents and additives conventionally used in rubber mixtures, such as plasticizers, pigments, antioxidants, sulfur, vulcanization accelerants, extender oils, one or more linking agents

of formulas other than (I) and/or one or more silica coating agents such as polyols, alkoxysilanes, in addition to the agent of formula (I). Preferably only one or more agents of formula (I) are used as silica coating agents, or if other linking agents are present, the weight of the linking agent or agents of formula (I) is greater than 50% of the weight of the total of linking agents.

The invention is illustrated in more detail by the following examples, which in no way limit the scope of the invention.

In the examples, the properties of the fillers, particularly of silica, and the properties of the compositions are evaluated as follows:

- Mooney viscosity: ML(1+4) at 100°C measured according to ASTP D-1646; it will be referred to below as "ML(1+4)100°."
- Elongation modulus at 300% (EM 300), 100% (EM 100) and 10% (EM 10), determined according to the standard ISO 37.
- Scott tear index measured at 20°C (hereinafter abbreviated as Scott20°), the rupture force (Fr) is expressed in MPa and the elongation at rupture (Er) is expressed in %.
- Hysteretic losses: Measured by rebound at 60°C, the deformation is of the order of 40%; these losses are referred to below as "HL", the word deformation being abbreviated to "def."
- Dynamic properties under shear, according to ASTM D2231-71 (reapproved in 1977), measurements carried out as a function of the deformation at 23°C and 10 Hz. The nonlinearity, expressed in MPa, which is the difference of shear modulus between

0.15% and 50% of the peak-to-peak deformation, is referred to below as "DeltaG\*."

The hysteresis is expressed by measurement of  $\text{tg}\delta$  and  $G''$  at 7% deformation.

In all the examples which follow, the values relating to the various components of the compositions -- unless otherwise indicated -- are given as parts by weight per 100 parts by weight of elastomer or mixture of elastomers (pce); the styrene contents of the polymers are expressed in % by mass, and the contents of 1,2-vinyl chains of the polymers are expressed in % relative to the butadiene units incorporated.

#### Example 1

The following basic formula F1 is used:

SBR	100
Silica (1)	80
Aromatic oil	40
Linking agent (2)	6.4
ZnO	2.5
Stearic acid	1.5
Antioxidant (6PPD)	1.9
Ozone wax C32T	1.5
Sulfur	1.1
Sulfenamide (CBS)	2
Diphenylguanidine	1.5

(1) = ZEOSIL 1165 silica (of Rhône-Poulenc)

(2) = Linking agent: Si69 of Degussa.

The abbreviation "SBR" represents a styrene-butadiene elastomer chosen from the group comprising the following three products, all of them solution-polymerized (SSBR).

SSBR A: 1.2 content = 41%; styrene content = 26%.

$T_g = -38^{\circ}\text{C}$ ;  $ML(1+4)_{100^{\circ}\text{C}} = 30$ ;

SSBR B: Same macro- and microstructure as SSBR A.

( $T_g = -38^{\circ}\text{C}$ ;  $ML(1+4)_{100^{\circ}} = 30$ ), but initiated with hexamethyleneiminolithium HMINLi (tertiary cycloaliphatic amine fixed at the end of the SBR chain).

SSBR C: Same macro- and microstructure as SSBR A

( $T_g = -38^{\circ}\text{C}$ ;  $ML(1+4)_{100^{\circ}} = 30$ ), but containing free dodecyl-hexamethyleneimine (DDCHMI) introduced just before the stripping stage, after stopping the polymerization.

The synthesis of these elastomers is carried out by a discontinuous process in the following manner.

#### Preparation of SSBR A

Into a 10-liter reactor containing 6.4 liters of de-aerated cyclohexane is injected 167 g of styrene, 476 g of butadiene and 1,500 ppm of THF. The impurities are neutralized with n-butyllithium, and 0.0035 mole of n-BuLi is then added, followed by 0.0019 mole of sodium tert.-butylate used as randomizing agent. The polymerization is carried out at  $55^{\circ}\text{C}$ .

At 98% conversion, the polymer is stopped by means of 0.0050 mole of methanol. The polymer solution is stirred for 15 minutes at  $55^{\circ}\text{C}$ .

The polymer is antioxidantized by the addition of 0.20 g per 100 g of elastomer (pce) of 2,2'-methylene bis-(4-methyl-6-tert.-butylphenol) and 0.20 pce of N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine. The solvent is eliminated by steam distillation and the polymer is dried on a cylindrical tool at 100°C.

The inherent viscosity of the product is 1.43 dL/g.

The percentage of styrene (<sup>1</sup>H NMR) is 26%; the amount of vinyl chains is 41%.

#### Preparation of SSBR B

SSBR B is prepared under conditions identical to those described for SBR A. with the exception that the initiation is done by means of 0.038 mole of hexamethyleneimine lithium, used in place of n-BuLi.

The inherent viscosity of the polymer is 1.45 dL/g.

#### ]Preparation of SSBR C

SSBR C is synthesized under conditions identical to those described for SSBR A, with the exception of the end of the reaction.

30 mEq./kg of dodecylhexamethyleneimine (0.8 pce) are added to the polymeric solution after the polymerization is stopped with methanol and before stripping the solvent by steam distillation.

Using the aforementioned elastomers, the following four compositions are prepared:

Composition 1: Formula F1 in which the SBR is SSBR A.

Composition 2: Formula F1, in which the SBR is SSBR B.

Composition 3: Formula F1 in which the SBR is SSBR C.

Composition 4: Formula F1 in which the SBR is SSBR A and which additionally contains 0.8 pce of free dodecylhexamethyleneimine (DDCHMI).

Composition 1 is a control composition, while Compositions 2, 3 and 4 are in conformity with the invention.

To prepare the mixtures which lead to the compositions, a two-stage thermomechanical operation is carried out which lasts 5 and 4 minutes, respectively, using an internal paddle mixer at an average paddle speed of 45 rpm, until attaining a maximum temperature of 160°C, whereas the finishing stage is performed at 30°C. In the case of Composition 4, the addition of the free amine (DDCHMI) is done with the aid of the internal mixer during the first stage of the thermomechanical operation.

All compositions are vulcanized at 150°C for 50 minutes.

The resulting properties of Compositions 1 to 4 in both the non-vulcanized state and the vulcanized state are compared with each other.

The results are listed in Table 1.

**Table 1**

Compositions	1	2	3	4
	F1	F1	F1	F1+0.8pce amine
	SSBR A	SSBR B	SSBR C	SSBR A
Initiator	nBuLi	HMIN1i	nBuLi	nBuLi
Stopper	MeOH	MeOH	MeOH+Amine	MeOH
	invention	invention	invention	
Properties in the nonvulcanized state:				
ML(1+4) 100°	51	55	54	51
Properties in the vulcanized state:				
Shore	64.0	58.8	56.5	59.4
EM10	5.10	3.83	3.48	3.95
EM 100	1.72	1.71	1.61	1.57
EM 300	2.03	2.26	2.19	1.96
EM300/EM100	1.18	1.32	1.36	1.25
Scott20° Fr	18.1	20.9	20.4	19.0
Er%	520	580	580	570
HL	33.2	25.1	26.1	29.4
(def = 40%)				
Dynamic properties under deformation (10Hz/def 0.15% - 50%):				
DeltaG*	4.05	1.09	1.03	1.95
tgδ	0.355	0.216	0.224	0.266
G"	1.230	0.433	0.436	0.690



Table 1 shows that the three compositions according to the invention, Compositions 2 to 4, have hysteretic properties that are considerably improved in comparison to the control composition 1, this being so both at low deformation ( $tg\delta$  values and  $G''$ ) and at high deformation (HL values), and that these compositions of the invention have reinforcing properties and rupture qualities that are considerably better than those of the control composition (EM300/EM100 and Scott20° values). Thus, this improvement can be obtained with a non-functionalized polymer (Compositions 3 and 4).

It is further noted that Composition 4, while being better than the control composition for the above reasons, has properties that are slightly poorer than those of Compositions 2 and 3, which shows that the introduction of the amine bonded to the polymer or perfectly dispersed in the elastomeric matrix by adding it in solution form before stripping is more effective for improving the hysteretic properties and mechanical cohesion.

### Example 2

The same basic formula F1 as in Example 1, and the following three SSBR's are used.

- SSBR D:  $T_g = -38^\circ\text{C}$ ; 1,2 content = 41%; styrene content = 26%;  $ML(1+4)_{100^\circ} = 70$
- SSBR E:  $T_g = -38^\circ\text{C}$ ; 1,2 content = 41%; styrene content = 26%; functionalized with hexamethylcyclotrisiloxane (D3);  $ML(1+4)_{100^\circ} = 60$

- SSBR F:  $T_g = -38^{\circ}\text{C}$ ; 1,2 content = 41%; styrene content = 26%; starved by means of tin tetrachloride;  $\text{ML}(1+4)100^{\circ} = 70$

- SSBR G:  $T_g = -38^{\circ}\text{C}$ ; 1,2 content = 41%; styrene content = 26%; functionalized with bis-diethylaminobenzophenone;  $\text{ML}(1+4)100^{\circ} = 70$

All these elastomers are synthesized by a continuous process, in the following manner:

#### Preparation of SSBR's D, E and G

Into a reactor of 14 L useful capacity and equipped with a turbine-type stirrer are continuously introduced cyclohexane, butadiene, styrene and tetrahydrofuran in mass proportions of 100 : 10.00 : 4.30 : 0.3, as well as a solution of n-butyllithium (SSBR D and G: 460 micromoles of active n-BuLi per 100 grams of monomers; SSBR E: 500 micromoles). The flow rates of these different solutions are calculated so that the dwelling time is 40 minutes under strong agitation. The temperature is kept constant at  $60^{\circ}\text{C}$ . At the exit from the reactor, the conversions measured on samples are 85% (SSBR D and G) and 88% (SSBR E). The three SBR's contain 26% incorporated styrene (by weight) and have a 1,2 bond content of 41% for the butadiene part.

SSBR D is stopped by means of methanol (MeOH/n-BuLi ratio = 1.5).

SSBR E is stopped by the addition of D3 (D3/n-BuLi ratio = 0.40).

SSBR G is stopped by the addition of bis-diethylaminobenzophenone (BDEAB/n-BuLi ratio = 1.5).

For the two polymers E and G, a contact time of 40 minutes between polymer and amine is assured by means of a second reactor stirred and heated at 60°C.

For the three elastomers, there is added 0.8 pce of 2,2'-methylene bis(4-methyl-6-tert.-butylphenol) and 0.2 pce of N-(1,3-dimethylbutyl)-N-phenyl-p-phenylenediamine used as antioxidants. The polymers are separated from the solvent by stripping the solvent by steam distillation, then dried on a 100°C tool for 10 minutes. The inherent viscosities (in toluene) are measured before the stripping operation.

The function content  $[\text{Si}(\text{CH}_3)_2\text{OH}]$  is determined by proton NMR assay.

The  $^1\text{H}$  NMR assay is carried out on a sample which has undergone three dissolution cycles in toluene, and coagulation in methanol, to eliminate any possible trace of residual hexamethylcyclotrisiloxane (not linked to the polymer). The molecular mass of SSBR E is  $175,000 \text{ g.mole}^{-1}$ .

The  $^1\text{H}$  NMR spectrum of dimethyl-silanol-functionalized SSBR E is characterized by peaks at 0.05 ppm and 0.1 ppm corresponding to the  $\text{Si}(\text{CH}_3)_2$  group. The content of  $[\text{Si}(\text{CH}_3)_2\text{OH}]$  units is 4.6 mEq./kg, or 81% of functionalized chains.

The amount of  $[(\text{C}_2\text{H}_5)_2\text{N}-\text{C}_6\text{H}_4]_2\text{COH}$  units of SSBR G is 5 mEq./kg, or 90% of functionalized chains. The molecular mass of SSBR G is  $180,000 \text{ g.mole}^{-1}$ .

### Preparation of SSBR F

SSBR F is synthesized under conditions analogous to those described for SSBR D and E, except for the amount of BuLi used and the mode of stoppage.

The amount of active n-BuLi is 900 micromoles per 100 grams of monomers.

At the exit from the reactor, the conversion is 92% (viscosity: 1.26 dL/g), the tin tetrachloride is injected upstream of a static mixer comprising 24 elements. The antioxidants are added 5 minutes after injection of  $\text{SnCl}_4$ .

The viscosity after stirring is 1.85 dL/g.

Eight compositions numbered 5 to 11 are prepared in the following manner:

Composition 5: Formula F1 in which the SBR is SSBR D;

Composition 6: Composition 5 to which 0.8 pce of DDCHMI has been added;

Composition 7: Formula F1 in which the SBR is SSBR E;

Composition 8: Composition 7 to which 0.8 pce of DDCHMI has been added;

Composition 9: Formula F1 in which the SBR is SSBR F;

Composition 10: Composition 9 to which 0.8 pce of DDCHMI has been added;

Composition 11: Formula F1 in which the SBR is SSBR G;

Composition 12: Composition 9 to which 0.8 pce of BDEAB has been added.

The preparation of the compositions by mixing, and their vulcanization, are carried out as in Example 1. For Compositions 6, 8, 10 and 11, the amine was added by means of an internal mixer during the first stage of the thermo-mechanical operation.

Compositions 5, 7, 9, 11 and 12 are control compositions, while Compositions 6, 8 and 10 are in conformity with the invention.

The tests are performed under the same conditions as in Example 1, and the results are listed in Table 2.

**Table 2**

Compositions	5	6	7	8	9	10	11	12
	F1	F1+amine 0.8pce	F1	F1+amine 0.8pce	F1	F1+amine 0.8pce	F1	F1+amine 0.8pce
DDCHMI								
	SSBR D		SSBR E		SSBR F		SSBR G	
Stopper	MeOH		D3		SnCl <sub>4</sub>		BDEAB	

Properties in the nonvulcanized state:

ML(1+4) 100°	79	76	87	86	43	42	85	80
--------------	----	----	----	----	----	----	----	----

Properties in the vulcanized state:

Shore	63.3	59.0	59.2	58.8	60.8	58.7	62.8	59.7
EM10	5.12	4.05	3.89	3.72	4.53	4.13	5.00	4.10
EM100	1.57	1.43	1.61	1.69	1.54	1.46	1.58	1.48
EM300	1.75	1.73	2.01	2.23	1.74	1.71	1.81	1.81
EM300/EM100	1.11	1.21	1.25	1.32	1.13	1.17	1.14	1.22
Scott20° Fr	21.1	20.9	24.0	25.0	17.6	18.1	21.6	21.8
Er%	650	680	610	590	600	620	610	640
HL	33.1	29.1	24.6	22.5	37.4	35.6	32.4	28.6

(def = 40%)

Dynamic properties under deformation (10Hz/def 0.15% - 50%):

DeltaG*	4.81	2.70	1.48	1.18	3.00	2.23	3.43	2.12
tgδ	0.370	0.281	0.249	0.228	0.336	0.305	0.321	0.265
G"	1.430	0.890	0.576	0.488	1.060	0.843	1.150	0.840

Compositions 6, 8 and 10 according to the invention show that the addition of free amine permits, with any functionalized or starred elastomer, to significantly improve the hysteresis and reinforcement compared with the properties obtained with the conventional compositions prepared without the addition of free amine, and even in comparison to those which comprise a polymer having aromatic dialkylamine functions at the chain end.

### Example 3

The following basic formulas F2 and F3 are used.

#### Formula F2

SBR	100
Silica (1)	60
Aromatic oil	20
Linking agent (2)	4.8
ZnO	2.5
Stearic acid	1.5
Antioxidant (6PPD)	1.9
Ozone wax C32T	1.5
Sulfur	1.1
Sulfenamide (CBS)	2
Diphenylguanidine	1.1

(1) = ZEOSIL 1165 silica (manufactured by Rhône-Poulenc)

(2) = Linking agent: Si69 (Degussa)

[illegible]

SBR	100
Silica (1)	40
N 234 Black	40
Aromatic oil	40
Linking agent (2)	3.2
ZnO	2.5
Stearic acid	1.5
Antioxidant (6PPD)	1.9
Ozone wax C32T	1.5
Sulfur	1.1
Sulfenamide (CBS)	2
Diphenylguanidine	0.8

(1) = ZEOSIL 1165 silica (manufactured by Rhône-Poulenc)

(2) = Linking agent: Si69 (Degussa).

With the aid of these two basic formulations, compositions were prepared using the elastomers SSBR A and SSBR B of Example 1.

These compositions are as follows:

Composition 11: Formula F2, with SSBR A as the SBR;

Composition 12: Formula F2, with SSBR B as the SBR;

Composition 13: Formula F2, with SSBR A as the SBR, and additionally containing 0.8 pce of DDCHMI;

Composition 14: Formula F3, with SSBR A as the SBR;

Composition 15: Formula F3, with SSBR B as the SBR.

Compositions 11 and 14 are control compositions, while Compositions 12, 13 and 15 are in conformity with the invention.

The preparation of the compositions by mixing and their vulcanization are carried out as in Example 1. The addition of the free amine to Composition 13 is done with the aid of the internal mixer during the first stage of this thermo-mechanical operation.

The results are listed in Tables 3 and 4.



Table 3

Compositions	11	12	13
Formula	F2	F2	F2+amine
Amine	0.8pceDDCHMI		
SSBR	SSBR A	SSBR B	SSBR A
Initiator	nBuLi	HMINLi	nBuLi
Stopper	MeOH	MeOH	MeOH
Properties in the nonvulcanized state:			
ML(1+4) 100°	64	78	69
Properties in the vulcanized state:			
Shore	64.2	57.2	55.3
EM10	5.41	3.68	3.38
EM 100	1.88	1.72	1.52
EM 300	2.20	2.44	2.13
EM300/EM100	1.17	1.42	1.40
Scott20° Fr	22.8	23.5	23.1
Er%	570	540	570
HL	27.2	18.9	22.8
(def = 35%)			
Dynamic properties under deformation (10Hz/def 0.15% - 50%):			
DeltaG*	3.07	0.39	0.38
tgδ	0.281	0.143	0.148
G"	0.878	0.247	0.252

Table 3 shows, in view of the properties in the vulcanized state, that the addition of free dodecylhexamethyleneimine (Composition 13) or the presence of hexamethyleneimine at the chain end (Composition 12) makes it possible to significantly improve the hysteresis and reinforcement in comparison to the properties obtained with the conventional Composition 11 which is not in conformity with the invention.

**Table 4**

Compositions	14	15
Formula	F3	F3
SSBR	SSBR A	SSBR B
Initiator	nBuLi	HMINLi
Stopper	MeOH	MeOH
Properties in the nonvulcanized state:		
ML(1+4) 100°	56	72
Properties in the vulcanized state:		
Shore	63.4	61.9
EM10	5.22	4.77
EM 100	1.62	1.75
EM 300	1.72	2.07
EM300/EM100	1.06	1.18
Scott20° Fr	17.8	19.0
Er%	650	580
HL	42.1	35.3
(def = 40%)		
Dynamic properties under deformation (10Hz/def 0.15% - 50%):		
DeltaG*	6.04	3.91
tgδ	0.421	0.365
G"	1.770	1.250

This table shows that, in the case of a filler based on carbon black and silica in a 50 : 50 mass proportion, the addition of amine to the elastomer chain improves the properties of hysteresis and reinforcement in comparison to the properties obtained with the corresponding control mixture 14 whose elastomer does not contain amine.

#### Example 4

In this example, the following four compositions are used.

Composition 16: Basic formula F1 in which the SBR is SSBR A;

Composition 17: Composition 16 wherein the DPG is replaced with 1.9 pce of dodecylhexamethyleneimine (DDCHMI), or 7.1 mmoles, the DDCHMI content in mmoles being the same as that of DPG in basic formula F1 (also 7.1 mmoles);

Composition 18: Composition 16 in which the DPG content is 2.5 pce (or 11.8 mmoles) instead of 1.50 pce (7.1 mmoles);

Composition 19: Composition 16, to which 1.2 pce (4.5 mmoles) of DDCHMI has been added.

Composition 19 is the only one that is in conformity with the invention;  
Compositions 16 to 18 are control compositions.

The compositions are prepared and vulcanized as in Example 1. The addition of amines in Compositions 17 and 19 is carried out with the aid of the internal mixer during the first stage of this thermomechanical operation.

The results are listed in Table 5.

**Table 5**

Compositions	16	17	18	19
Formula	F1	F1	F1	F1
DPG (PCE) (mmol)	1.50 (7.1)	0	2.5 (11.8)	1.5 (7.1)
DDCHMI ADDED (PCE)	0	1.9 (7.1)	0	1.2 (4.5)

Properties in the nonvulcanized state:

ML(1+4)100°	51	46	47	54
-------------	----	----	----	----

Properties in the vulcanized state:

Shore	64.0	63.3	62.8	60.0
EM10	5.10	5.17	4.32	4.15
EM 100	1.72	1.50	1.89	1.65
EM 300	2.03	1.57	2.59	2.07
EM300/EM100	1.18	1.05	1.37	1.25
Scott20° Fr	18.1	18.3	20.4	20.8
Er%	520	670	500	560
HL	33.2	38.4	26.2	29.3

(def = 35%)

Dynamic properties under deformation (10Hz/def 0.15% - 50%):

DeltaG*	4.05	3.43	2.71	1.64
tgδ	0.355	0.308	0.306	0.254
G"	1.230	1.050	0.872	0.605

This example shows that the most effective composition for reducing the hysteresis at low deformations is the composition in which both DPG and DFDCHMI are present (Composition 19).

#### Example 5

The following four compositions are used:

Composition 20: Basic formula F1 where the SBR is SSBR A;

Composition 21: Composition 20 to which 0.4 pce (2.2 mmoles) of dicyclohexylamine (DCHA) has been added;

Composition 22: Composition 20 to which 0.8 mmoles (3.8 mmoles) of DCHA has been added;

Composition 23: Composition 20 to which 0.8 pce (3 mmoles) of DDCHMI has been added.

Composition 20 is the control composition, while Compositions 21 to 23 are in conformity with the invention.

The compositions are prepared and vulcanized as in Example 1. The addition of the amines for Compositions 21, 22 and 23 is done with the aid of the internal mixer during the first stage of this thermomechanical operation.

The results are given in Table 6.

**Table 6**

Compositions	20	21	22	23
Formula	F1	F1	F1	F1
DCHA (pce) (mmoles)	0	0.4/2.2	0.8/3.8	
DDCHMI ADDED (pce/mmmoles)	0	0	0	0.8/3
Properties in the nonvulcanized state:				
ML(1+4)100°	51	51	50	51
Properties in the vulcanized state:				
Shore	64.0	63.1	61.8	59.4
EM10	5.10	4.78	4.79	3.95
EM 100	1.72	1.70	1.72	1.57
EM 300	2.03	2.03	2.06	1.96
EM300/EM100	1.18	1.19	1.20	1.25
Scott20° Fr	18.1	19.8	20.3	19.0
Er%	520	550	560	570
HL	33.6	30.5	30.3	29.4
(def = 35%)				
Dynamic properties under deformation (10Hz/def 0.15% - 50%):				
DeltaG*	4.05	3.42	3.23	1.95
tgδ	0.355	0.327	0.322	0.266
G"	1.230	1.070	1.010	0.690

This example shows that addition of amines DCHA and DDCHMI makes it possible to reduce the hysteresis at low and high deformations in comparison to the control. However, DDCHMI (Composition 23) is more effective.

#### Example 6

The following compositions are used:

Composition 24: Formula F1 where the SBR is SSBR A;

Composition 25: Composition 24 to which 0.8 pec of DDCHMI has been added;

Composition 26: Composition 24 where 5.7 pce of Si266 made by Degussa (bispropyltriethoxysilane disulfide) was used instead of 6.4 pce of Si69;

Composition 27: Composition 26, which additionally contains 0.8 pce of DDCHMI.

Compositions 25 and 27 are prepared according to the invention; Compositions 24 and 26 are control compositions.

The compositions are prepared and vulcanized as in Example 1. For Compositions 25 and 27 the amines are added with the aid of the internal mixer during the first stage of this thermomechanical operation.

The results are listed in Table 7.



**Table 7**

Compositions	24	25	26	27
Formula	F1	F1	F1	F1
Si69 (pce)	6.4	6.4	0	0
Si266 (pce)	0	0	5.7	5.7
DDCHMI (pce)	0	0.8	0	0.8
Properties in the nonvulcanized state:				
ML(1+4)100°	51	51	49	48
Properties in the vulcanized state:				
Shore	64.0	59.4	59.0	58.2
EM10	5.10	3.95	4.09	4.01
EM 100	1.72	1.57	1.20	1.18
EM 300	2.03	1.96	1.19	1.11
EM300/EM100	1.18	1.25	0.99	0.94
Scott20° Fr	18.1	19.0	16.1	15.0
Er%	520	570	720	750
HL	33.2	29.4	42.8	44.1
(def = 35%)				
Dynamic properties under deformation (10Hz/def 0.15% - 50%):				
DeltaG*	4.05	1.95	2.68	2.38
tgδ	0.355	0.266	0.312	0.295
G"	1.230	0.690	0.905	0.818

This example shows that the addition of DDCHMI permits a major improvement of hysteresis at low deformations in the case of a linking agent that is in conformity with the invention (Si69 or Si266), and that the use of Si69 (comprising four sulfur atoms in the molecule) gives better results with regard to hysteresis at low and high deformations and with regard to reinforcement than does the use of Si266 which only has two sulfur atoms in its molecule.

### Example 7

The following compositions are used:

Composition 28: Formula F1 in which the SBR is SSBR A;

Composition 29: Formula F1 in which the SBR is SSBR B;

Composition 30: Composition 29 which only contains 3.2 pce of Si69;

Composition 31: Composition 29 devoid of linking agent;

Composition 32: Formula F1 in which the SBR is SSBR C;

Composition 33: Composition 32, in which the Si69 content is only 3.2 pce;

Composition 34: Composition 32 devoid of linking agent.

Compositions 29, 30, 32 and 33 are in accordance with the invention;

Compositions 28, 31 and 34 are control compositions.

The compositions are prepared and vulcanized as in Example 1.

The results are given in Table 8.

**Table 8**

Compositions	28	29	30	31	32	33	34
Formula	F1	F1	F1	F1	F1	F1	F1
Si69 (pce)	6.4	6.4	3.2	0	6.4	3.2	0
SSBR	A	B	B	B	C	C	C
Properties in the nonvulcanized state:							
ML(1+4)100°	51	55	68	147	54	59	132
Properties in the vulcanized state:							
Shore	64.0	58.8	60.0	66.8	56.5	59.2	65.0
EM10	5.10	3.83	4.64	7.65	3.48	4.33	7.28
EM 100	1.72	1.71	1.36	0.94	1.61	1.37	0.78
EM 300	2.03	2.26	1.52	0.52	2.19	1.59	0.41
EM300/EM100	1.18	1.32	1.12	0.55	1.36	1.16	0.53
Scott20° Fr	18.1	20.9	18.0	8.0	20.4	18.6	7.1
Er%	520	580	720	1030	580	680	1020
HL	33.2	25.1	33.5	54.7	26.1	33.7	59.9
(def = 35%)							
Dynamic properties under deformation (10Hz/def 0.15% - 50%):							
DeltaG*	4.05	1.09	1.74	4.32	1.03	1.77	5.15
tgδ	0.355	0.216	0.242	0.263	0.224	0.252	0.297
G"	1.230	0.433	0.590	1.110	0.436	0.618	1.390

This example shows that the presence of amino groups is not sufficient to improve the compromise between hysteretic properties and mechanical cohesion; also necessary is the presence of a linking agent according to Formula (I), and the content of linking agent or ensemble of linking agents in accordance with this formula should preferably be at least equal to 4% by weight of the content of the silica or ensemble of silicas, which is the case in Compositions 29, 30, 32 and 33; the results are better for Compositions 29 and 32 where the linking agent content is more than 4 % of the weight of silica.

It is to be understood that the invention is not limited to the above-described embodiments, on the basis of which it is possible to envisage other modes of carrying out the invention.

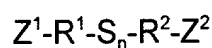
## CLAIMS

1. Rubber composition vulcanizable with sulfur, characterized in that it comprises

a) at least one polymer selected from the group consisting of diene polymers, olefin/monomeric diene copolymers and halogenated isoolefin/para-alkylstyrene copolymers;

b) silica as filler;

c) at least one agent promoting linking between silica and polymer, said agent having the formula (I)

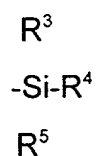


wherein

n is an integer between 2 and 8,

R<sup>1</sup> and R<sup>2</sup>, which may be the same or different, are each selected from the collectives consisting of substituted or unsubstituted alkylene groups having a total of 1 to 18 carbon atoms and of substituted or unsubstituted arylene groups having a total of 6 to 12 carbon atoms,

Z<sup>1</sup> and Z<sup>2</sup>, which may be the same or different, each represents a group



where R<sup>3</sup>, R<sup>4</sup> and R<sup>5</sup>, which may be the same or different, are each selected from the collective comprising alkyl groups having 1 to 4 carbon atoms, phenyl groups, alkoxy groups having 1 to 8 carbon atoms, and cycloalkoxy groups having 5 to 8 carbon atoms, on condition that at least one of R<sup>3</sup>, R<sup>4</sup> and R<sup>5</sup> is an alkoxy or cycloalkoxy;

d) at least one guanidine substituted by at least two groups which may be the same or different and each selected from the collective comprising alkyl, aryl or aralkyl groups;

and in that it has at least one of the following characteristics:

- It comprises at least one diene polymer which has at least one amino terminal group of an aliphatic or cycloaliphatic amine which is bonded thereto at the end of the chain, the polymer then being devoid of alkoxysilane and silanol group;
- the composition comprises at least one free aliphatic or cycloaliphatic amine.

2. Composition according to Claim 1, characterized in that the filler consists entirely of silica, or contains at least 40% by weight of silica, or preferably at least 50% by weight of silica.

3. Composition according to either one of Claims 1 or 2, characterized in that in the linking agent of formula (1), n is greater than 2, or if there are several such agents, at least 80% of n is greater than 2 for the total of these compounds.

4. Composition according to any one of Claims 1 to 3, characterized in that the content of agent of formula (1) or mixture of such agents is at least 4% by weight calculated on the weight of silica or mixture of silicas used as filler.

5. Composition according to any one of Claims 1 to 4, characterized in that the content of guanidine or mixture of guanidines is 0.5 to 4% by weight calculated on the weight of silica or total of silicas, said content preferably ranging from 1 to 3% by weight.

6. Composition according to any one of Claims 1 to 5, characterized in that the content of free aliphatic or cycloaliphatic amine, or mixture of free aliphatic or cycloaliphatic amines, is in the range of 0.5 to 4% by weight calculated on the weight of silica or total of silicas, said content advantageously being 1 to 3% by weight.

7. Composition according to any one of Claims 1 to 6, characterized in that it comprises at least one free aliphatic or cycloaliphatic amine homogeneously dispersed in the composition.

8. Composition according to Claim 7, characterized in that the polymer is prepared in solution and that the aliphatic or cycloaliphatic amine is introduced into this solution after stopping the polymerization and before stripping of the solvent.

9. Tread of tire casing comprising at least one composition according to any one of Claims 1 to 8.

10. Tread obtained by vulcanization of the tread according to Claim 9.

11. Tire casing comprising at least one composition according to any one of Claims 1 to 8.

12. Tire casing obtained by vulcanizing the tire according to Claim 11.

**CAS P10-1005**

**COMPANY NAMED:** COMPAGNIE GENERALE DES ETABLISSEMENTS

**MICHELIN- MICHELIN ET CIE**

**Title:** SILICA-CONTAINING RUBBER COMPOSITION

**VULCANIZABLE WITH SULFUR**

**ABSTRACT**

Rubber composition vulcanizable with sulfur, characterized in that it comprises:

a) at least one polymer selected from the group consisting of diene polymers, olefin/monomeric diene copolymers and isoolefin/halogenated para-alkylstyrene copolymers;

b) silica as filler;

c) at least one agent of the sulfur-containing silane type promoting the linkage between silica and polymer;

d) at least one substituted guanidine;

and in that it has at least one of the following characteristics:

- It has at least one diene polymer which comprises at least one terminal amino group of an aliphatic or cycloaliphatic amine which is bonded thereto at the end of the chain, the polymer then being devoid of the alkoxysilane and silanol group;
- the composition comprises at least one free aliphatic or cycloaliphatic amine.

Tire tread and tire casing comprising such a composition.



FILE NO.: A32851-PCT-USA  
070338.0556  
PATENT

TO ALL WHOM IT MAY CONCERN:

Be it known that WE, Marc Daniel and Gérard Labauze, both citizens of France, whose post office addresses are: 125 River Way Drive, Greer, South Carolina, USA; and 3, rue du Parc de Montjuzet, F-63100 Clermont-Ferrand, France, respectively, have invented an improvement in

SILICA-CONTAINING RUBBER COMPOSITION  
VULCANIZABLE WITH SULFUR

of which the following is a

SPECIFICATION

BACKGROUND OF INVENTION

The present invention relates to elastomer compositions comprising silica as reinforcing filler, said compositions having improved hysteretic properties in the vulcanized state.

Since economizing on fuel and protection of the environment have become priorities, it is desirable to produce mixtures having the lowest possible hysteresis, in order to be able to use them as semi-finished products which enter into the make-up of tire casings, semi-finished products such as undercoats, binding gums between rubbers of different types, or for calendering metallic or textile reinforcements, sidewall gums or treads, and to obtain tires with improved properties, said tires having a reduced resistance to rolling in particular.

To achieve this objective, numerous solutions have been proposed consisting, in particular, in modifying the nature of the diene polymers and copolymers at the end of polymerization by means of coupling agents, starring agents or functionalizing agents. The

great majority of these solutions are essentially concentrated on the use of polymers modified with carbon black as reinforcing filler, with a view to obtaining a good interaction between the modified polymer and the carbon black, since the use of white reinforcing agents, notably silica, has proved inappropriate owing to the low value of some of its properties, and, as a result, of certain properties of the tires using these compositions.

As an illustrative example from the prior art, mention may be made of U.S. Patent 4,677,165, which describes the reaction of living diene polymers functionalized by means of a benzophenone derivative to obtain polymers having improved properties in compositions containing carbon black as reinforcing filler. EP-A-0,451,604 describes, as functionalizing agent, a compound having an amino function which permits an improved interaction between the modified polymers and carbon black. With the same objective, U.S. Patent 4,647,625 describes the functionalization of elastomers by reaction of a living polymer with N-methylpyrrolidine. EP-A-0,590,491 and EP-A-0,593,049 describe polymers having a tertiary amino function at the end of the chain and also permitting better interaction with carbon black.

Certain solutions have also been proposed concerning the use of silica as reinforcing filler in the compositions designed to constitute treads of tires. Functionalized polymers comprising alkoxysilane functions at the end of the polymer chains, as described in EP-A-0,299,074 and EP-A-0,447,066, have been proposed for this purpose. It is only these functionalized polymers that have been described in the prior art as being effective in reducing

the hysteresis and improving the resistance to abrasion, but the industrial manufacture of these polymers poses problems due to macrostructure development during the recovery stages such as stripping or drying. To attempt to solve these problems, the use of polymers functionalized with non-hydrolyzable alkoxysilane functions, as described in U.S. Patent 5,066,721 have been proposed, but their effectiveness in a mixture with silica is reduced. The preparation of diene polymers having an amino function is known to persons skilled in the art, e.g. from U.S. Patent 4,894,409, which describes the preparation of polymers functionalized with aromatic amines. The polymers having an amine function are not very effective when used with silica, as mentioned in EP-A-0,661.298.

This interest in silica-reinforced compositions was revived with the publication of EP-A-0,501,227 which discloses a rubber composition vulcanizable with sulfur, obtained by thermomechanical working of a copolymer of a conjugated diene and a vinylaromatic compound, prepared by solution polymerization, with 30 to 150 parts by weight per 100 parts by weight of elastomer of a particular precipitated silica, which represents an excellent compromise between several contradictory properties, and which for the first time permits the commercialization of tires possessing a silica-filled tread showing the excellent compromise that is required.

Mention may also be made of European Patent document EP-A-819,731, which discloses a silica-reinforced composition essentially comprising a diene elastomer consisting of a copolymer having amino functions and a silica/elastomer linking agent of the sulfurated silane

type. Along its chain, this copolymer has amino groups originating from nonaliphatic or cycloaliphatic amines and an aminated vinylaromatic monomer.

It will be noted that the problem that is supposed to be solved in this last document does not relate to obtaining improved hysteretic properties.

SUMMARY OF THE INVENTION

The present invention relates to a new rubber composition containing silica or a mixture of silica and carbon black as reinforcing filler, said composition having satisfactory properties when used in the crude state and improved properties in the vulcanized state, particularly an excellent hysteresis and excellent reinforcement.

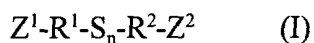
The invention also relates to treads of tires comprising at least one composition in accordance with the invention, as well as to treads obtained by vulcanization of these treads.

The invention also relates to casings of tires comprising at least one composition according to the invention, as well as to tire casings obtained by vulcanization of these casings, at least one composition of the invention being used, e.g., in the tread.

The rubber composition vulcanizable with sulfur, according to the invention, is characterized in that it comprises:

- a) at least one polymer selected from the group consisting of diene polymers, olefin/monomeric diene copolymers and halogenated isoolefin/para-alkylstyrene copolymers;

- b) silica as filler;
- c) at least one agent promoting binding between silica and polymer, said agent having the formula

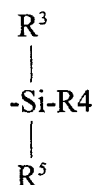


wherein

n is an integer between 2 and 8,

R<sup>1</sup> and R<sup>2</sup>, which may be the same or different, are each selected from among substituted or unsubstituted alkylene groups having 1 to 18 carbon atoms and substituted or unsubstituted arylene groups having 6 to 12 carbon atoms,

Z<sup>1</sup> and Z<sup>2</sup>, which may be the same or different, each represents a group



where R<sup>3</sup>, R<sup>4</sup> and R<sup>5</sup>, which may be the same or different, are each selected from among alkyl groups having 1 to 4 carbon atoms, phenyl groups, alkoxy groups having 1 to 8 carbon atoms, and cycloalkoxy groups having 5 to 8 carbon atoms, with the proviso that at least one of R<sup>3</sup>, R<sup>4</sup> and R<sup>5</sup> is an alkoxy or cycloalkoxy; and

- d) at least one guanidine substituted by at least two groups, which may be the same or different, and selected from among alkyl, aryl or aralkyl groups;

and wherein the rubber composition has at least one of the following characteristics:

- It comprises at least one diene polymer which has at least one terminal amino group of an aliphatic or cycloaliphatic amine which is bonded thereto at the end of the chain, the polymer then being devoid of alkoxysilane and silanol group;

- The composition comprises at least one free aliphatic or cycloaliphatic amine.

#### Detailed Description of the Invention

In the description that follows, the term "polymer" covers both homopolymers and copolymers; the term "copolymer" referring to polymers obtained from two or more than two monomers, e.g. terpolymers.

Understood by a diene polymer is any homopolymer obtained by polymerization of a conjugated diene monomer having 4 to 12 carbon atoms, any copolymer obtained by copolymerization of one or more conjugated diene with each other or with one or more vinylaromatic compounds having 8 to 20 carbon atoms. As conjugated diene, mention may be made of e.g. 1,3-butadiene, 2-methyl-1,3-butadiene, 2,3-di(C<sub>1</sub>-C<sub>5</sub>-alkyl)-1,3-butadiene such as, e.g., 2,3-dimethyl-1,3-butadiene, 2,3-diethyl-1,3-butadiene, 2-methyl-3-ethyl-1,3-butadiene, 2-methyl-3-isopropyl-1,3-butadiene, phenyl-1,3-butadiene, an aryl-1,3-butadiene, 1,3-pentadiene, and 2,4-hexadiene.

Suitable vinylaromatic compounds are, in particular, styrene, ortho-, meta- and paramethylstyrene, the commercial "vinyl-toluene" mixture, p-tert.-butylstyrene, the

methoxystyrenes, chlorostyrenes, vinylmesitylene, divinylbenzene, and vinylnaphthalene.

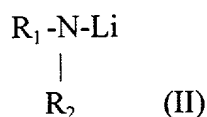
The copolymers may contain, e.g., between 99% and 20% by weight of diene units and from 1% to 80% by weight of vinylaromatic units. The polymers may have any microstructure, which is a function of the polymerization conditions used, notably of the presence or absence of a modifying agent and/or randomizing agent and of the amounts of modifying and/or randomizing agent used.

Polybutadienes are preferred, particularly those having a 1,2-linkage content of between 1% and 80%, as well as polyisoprenes, and copolymers of butadiene and styrene in particular, those having a styrene content of between 5 and 50% by weight, and more particularly between 20% and 40% by weight, a 1,2-linkage content of the butadiene part of between 4% and 65%, and a trans-1,4 linkage content of between 30% and 80%. Suitable butadiene-styrene-isoprene copolymers are those having a styrene content of between 5 and 50% by weight, more particularly between 10% and 40%, an isoprene content of between 15% and 60% by weight, more particularly between 20% and 50% by weight, and a butadiene content of between 5% and 50% by weight, more particularly between 20% and 40% by weight, wherein the butadiene part has a 1,2-linkage content of between 4% and 85% and a trans-1,4 linkage content of between 6% and 80%, and the isoprene part has a 1,2-linkage content plus 3,4-linkage content of between 5% and 70% and a trans-1,4-linkage content of between 10% and 50%.

When the diene polymer has an amino terminal group, it is then devoid of an

alkoxysilane group and silanol group and may be a homopolymer or copolymer obtained from the above-mentioned monomers, wherein said polymer can be obtained by initiation or functionalization.

In the case where the terminal amino group is introduced by initiation, the polymerization is advantageously carried out with an initiator of the lithium amide type, as described in the literature, e.g. in the work of T.C. Cheng, "Anionic Polymerization," published by the American Chemical Society, Washington, p. 513, 1981, whose content is incorporated herein. This lithium amide, has the formula



wherein  $R_1$  and  $R_2$ , independently of one another, are an alkyl group, or together form a cycloalkyl, the number of carbon atoms of the compound formed by  $R_1$  and  $R_2$  preferably being 2 to 15.

As a preferred example,  $R_1$  and  $R_2$  may each be an ethyl or butyl group, or together form a cycloalkyl radical having 4 to 6 carbon atoms.

When necessary, the initiator of formula (II) is prepared in the presence of a polar agent such as tetrahydrofuran, by reacting the corresponding amine  $R_1-NH-R_2$ , such as hexamethyleneimine, with an alkyl lithium, such as n-butyllithium.

In the case where the amino end group is introduced by functionalization at the end of



polymerization, the functionalization procedures described in, e.g., EP-A-451,604, U.S. Patent 4,647,625 or in Kenji Ueda et al., "Synthesis of polymers with amino end groups. 3. Reactions of anionic living polymers with  $\alpha$ -halo- $\omega$ -aminoalkanes with a protected amino functionality," Macromolecules 23: 939-945 (1990), may be used.

5           The polymerization may be carried out by a continuous or a discontinuous process. The polymerization is generally carried out at a temperature between 20°C and 120°C, preferably between 30°C and 90°C.

10           The olefin/diene copolymers can be, notably, EPDM's (ethylene-propylene-diene monomer), such as ethylene-propylene-1,4-hexadiene copolymers, ethylene-propylene-ethylidenenorbornene copolymers, ethylene-propylene-dicyclopentadiene copolymers, butyl rubbers, particularly isobutylene-halogenated isoprene copolymers, as the case may be. The isoolefin/ halogenated para-alkylstyrene copolymers can be, e.g. the isobutylene-/ halogenated para-methylstyrene rubber marketed by Exxon under the trade name EXXPRO.

15           The polymers may be, e.g., block polymers, statistical polymers, sequenced polymers, microsequenced polymers, and can be prepared by dispersion polymerization, solution polymerization, bulk polymerization, or in a gaseous phase.

          The composition according to the invention may comprise a mixture of two or more polymers defined above.

          The free aliphatic or cycloaliphatic amine may be a primary, secondary or tertiary amine.

By way of nonlimiting examples, mention may be made, e.g., of the following amines: butyl, dibutyl, tributylamines, pentyl, dipentyl, tripentylamines, hexyl, dihexyl, trihexylamines, cyclohexyl, dicyclohexyl, tricyclohexyl amines, benzyl, dibenzyl, tribenzylamines, octyl, dioctyl, trioctylamines, decyl, didecylamines, dodecyl, didodecylamines, pyrrolidine and alkyl pyrrolidines, piperidine and alkylpiperidines, hexamethyleneimine and alkylhexamethyleneimines, wherein said amines may be used alone or in a mixture with one another.

Preferably, the free amine content or the mixture of free amines ranges from 0.5 to 4% by weight calculated on the total weight of silicas, said content advantageously being between 1 and 3% by weight.

The substituted guanidine may be, e.g., triphenylguanidine, diphenylguanidine, or di-o-tolylguanidine. The composition may comprise a mixture of two or more substituted guanidines.

The content of substituted guanidine or mixture of substituted guanidines is 0.5 to 4% by weight calculated on the silica or total of silicas, said content advantageously being 1 to 3% by weight.

The silica used as filler may be any silica known to persons skilled in the art having a BET surface of less than or equal to 450 m<sup>2</sup>/g, a specific surface area CTAB of less than or equal to 450 m<sup>2</sup>/g, even though this improvement is more pronounced with a highly dispersible precipitated silica. Understood by the term "highly dispersible silica" is any silica capable of

deagglomeration and dispersion in a very large amount of polymeric matrix, observable on fine sections by electron microscopy or optical microscopy. Nonlimiting examples of such preferred, highly dispersible silicas are those obtained according to the processes described in EP-A-0,157,703 and EP-A-0,520,862, or the Zeosil silica 1165 MP of Rhône-Poulenc, the Perksasil silica KS 430 of Akzo, silica Hi-Sil 2000 of PPG, and silicas Zeopol 8741 and Zeopol 8745 of Huber Co. According to the invention, the beneficial effect is obtained regardless of the physical state in which the silica is present, i.e whether it is in powder form, micropearl form, granulated form, spherical form, and regardless of what the specific surface area of the silica is. It is also possible to use blends of different silicas and use other white fillers, such as chalk, kaolin or alumina.

In combination with silica, it is possible, if necessary, to use carbon black in the reinforcing filler, notably all carbon blacks that are commercially available or conventionally used in tires, particularly in treads.

The filler comprises one or more silicas or it contains at least 40% by weight – and advantageously at least 50% by weight – a silica or mixture of silicas.

The reinforcing filler, which may thus comprise silica without carbon black or both silica and carbon black, is present in the composition in an amount which may range, e.g., from 30 to 100 parts by weight of the polymer or mixture of polymers.

By way of examples of an agent of formula (I) which promotes linking between the silica

or combination of silicas and the diene polymer or mixture of diene polymers, mention may be made of the 2,2'-bis(trimethoxysilylethyl) polysulfides, the 3,3'-bis(trimethoxysilylpropyl) polysulfides, the 3,3'-bis (triethoxysilylpropyl) polysulfides, the 2,2'-bis(triethoxysilylpropyl) polysulfides, the 2,2'-bis(tripropoxysilylethyl) polysulfides, the 2,2'-bis(tri-sec-butoxysilylethyl) polysulfides, the 3,3'-bis(tri-tert-butoxyethyl) polysulfides, the 3,3'-bis (triethoxysilylethyltolylene) polysulfides, the 3,3'-bis(trimethoxy-silylethyltolylene) polysulfides, the 3,3'-bis(trisopropoxypropyl) polysulfides, the 3,3'-bis (trioctoxypropyl) polysulfides, the 2,2'-bis(2'-ethylhexoxysilylethyl) polysulfides, the 2,2'-bis(dimethoxy-ethoxysilylethyl) polysulfides, the 3,3'-bis(methoxyethoxypropoxysilylpropyl) polysulfides, the 3,3'-bis(methoxydimethylsilylpropyl) polysulfides, the 3,3'-bis(cyclohexoxydimethylsilylpropyl) polysulfides, the 4,4'-bis(trimethoxy-silylbutyl) polysulfides, the 3,3'-bis(trimethoxysilyl-3-methylpropyl) polysulfides, the 3,3'-bis(tripropoxysilyl-3-methylpropyl) polysulfides, the 3,3'-bis(trimethoxymethylsilyl-3-ethylpropyl) polysulfides, the 3,3'-bis(trimethoxy-silyl-2-methylpropyl) polysulfides, the 3,3'-bis(dimethoxyphenylsilyl-2-methylpropyl) polysulfides, the 3,3'-bis(trimethoxysilylcyclohexyl) polysulfides, the 12, 12'-bis(trimethoxysilyldodecyl) polysulfides, the 12, 12'-bis(triethoxysilyl-dodecyl) polysulfides, the 18, 18'-bis(trimethoxysilyloctadecyl) polysulfides, the 18, 18'-bis(methoxydimethylsilyloctadecyl) polysulfides, the 2,2'-bis(trimethoxysilyl-2-methylethyl) polysulfides, the 2,2'-bis(triethoxysilyl-2-methylethyl) polysulfides, the 2,2'-bis(tripropoxysilyl-2-methylethyl)

polysulfides, and the 2,2'-bis(trioctoxysilyl-2-methylethyl) polysulfides. Such a linking agent is, e.g., that sold by Degussa under the trade designation Si69 whose average formula is bis(3-triethoxysilylorioyl) tetrasulfide. These polysulfides can be used alone or in a mixture with each other.

5 By preference, n in the linking agent of formula (I) is greater than 2, or if there are several such agents, at least 80% of n is greater than 2 for the total of these compounds.

The content of the agent of formula (I) or mixture of such agents is preferably at least 4% of the weight of silica or of the mixture of silicas used as filler.

10 The compositions according to the invention can also contain other constituents and additives conventionally used in rubber mixtures, such as plasticizers, pigments, antioxidants, sulfur, vulcanization accelerants, extender oils, one or more linking agents of formulas other than (I) and/or one or more silica coating agents such as polyols, alkoxysilanes, in addition to the agent of formula (I). Preferably only one or more agents of formula (I) are used as silica coating agents, or if other linking agents are present, the weight of the linking agent or agents of formula  
15 (I) is greater than 50% of the weight of the total of linking agents.

The invention is illustrated in more detail by the following examples, which in no way limit the scope of the invention.

In the examples, the properties of the fillers, particularly of silica, and the properties of the compositions are evaluated as follows:

- Mooney viscosity: ML(1+4) at 100°C measured according to ASTP D-1646; it will be referred to below as “ML(1+4)100°.”

- Elongation modulus at 300% (EM 300), 100% (EM 100) and 10% (EM 10), determined according to the standard ISO 37.

5 - Scott tear index measured at 20°C (hereinafter abbreviated as Scott20°), the rupture force (Fr) is expressed in MPa and the elongation at rupture (Er) is expressed in %.

- Hysteretic losses: Measured by rebound at 60°C, the deformation is of the order of 40%; these losses are referred to below as “HL”, the word deformation being abbreviated to “def.”

10 - Dynamic properties under shear, according to ASTM D2231-71 (reapproved in 1977), measurements carried out as a function of the deformation at 23°C and 10 Hz. The nonlinearity, expressed in MPa, which is the difference of shear modulus between 0.15% and 50% of the peak-to-peak deformation, is referred to below as “DeltaG\*.” The hysteresis is expressed by measurement of  $\text{tg}\delta$  and  $G''$  at 7% deformation.

15 In all the examples which follow, the values relating to the various components of the compositions -- unless otherwise indicated -- are given as parts by weight per 100 parts by weight of elastomer or mixture of elastomers (pce); the styrene contents of the polymers are expressed in % by mass, and the content of 1,2-vinyl chains of the polymers is expressed in % relative to the butadiene units incorporated.

Example 1

The following basic formula F1 is used:

SBR	100
Silica (1)	80
Aromatic oil	40
Linking agent (2)	6.4
ZnO	2.5
Stearic acid	1.5
Antioxidant (6PPD)	1.9
Ozone wax C32T	1.5
Sulfur	1.1
Sulfenamide (CBS)	2
Diphenylguanidine	1.5

(1) = ZEOSIL 1165 silica (Rhône-Poulenc)

(2) = Linking agent: Si69 (Degussa)

The abbreviation "SBR" represents a styrene-butadiene elastomer chosen from the group comprising the following three products, all of them solution-polymerized (SSBR).

SSBR A: 1,2 content = 41%; styrene content = 26%.

T<sub>g</sub> = - 38°C; ML(1+4)100°C = 30;

SSBR B: Same macro- and microstructure as SSBR A.

( $T_g = -38^\circ\text{C}$ ;  $ML(1+4)_{100^\circ} = 30$ ), but initiated with hexamethyleneiminolithium HMINLi (tertiary cycloaliphatic amine fixed at the end of the SBR chain).

SSBR C: Same macro- and microstructure as SSBR A

( $T_g = -38^\circ\text{C}$ ;  $ML(1+4)_{100^\circ} = 30$ ), but containing free dodecyl-hexamethyleneimine (DDCHMI) introduced just before the stripping stage, after stopping the polymerization.

The synthesis of these elastomers is carried out by a discontinuous process in the following manner.

#### Preparation of SSBR A

Into a 10-liter reactor containing 6.4 liters of de-aerated cyclohexane is injected 167 g of styrene, 476 g of butadiene and 1,500 ppm of THF. The impurities are neutralized with n-butyllithium, and 0.0035 mole of n-BuLi is then added, followed by 0.0019 mole of sodium tert-butyrate used as randomizing agent. The polymerization is carried out at  $55^\circ\text{C}$ .

At 98% conversion, polymerization is stopped by adding 0.0050 mole of methanol. The polymer solution is stirred for 15 minutes at  $55^\circ\text{C}$ .

The polymer is antioxidantized by the addition of 0.20 g per 100 g of elastomer (pce) of 2,2'-methylene bis-(4-methyl-6-tert-butylphenol) and 0.20 pce of N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine. The solvent is eliminated by steam distillation and the polymer is



dried on a cylindrical tool at 100°C.

The inherent viscosity of the product is 1.43 dL/g.

The percentage of styrene (<sup>1</sup>H NMR) is 26%; the amount of vinyl chains is 41%.

#### Preparation of SSBR B

5 SSBR B is prepared under conditions identical to those described for SBR A, with the exception that polymerization is accomplished by the addition of 0.038 mole of hexamethyleneimine lithium (HMINLI), used in place of n-BuLi.

The inherent viscosity of the polymer is 1.45 dL/g.

#### Preparation of SSBR C

10 SSBR C is synthesized under conditions identical to those described for SSBR A, with the exception of the end of the reaction. 30 mEq./kg of dodecylhexamethyleneimine (DDCHMI) (0.8 pce) are added to the polymeric solution after the polymerization is stopped with methanol and before stripping the solvent by steam distillation.

Using the aforementioned elastomers, the following four compositions are prepared:

15 Composition 1: Formula F1 in which the SBR is SSBR A.

Composition 2: Formula F1, in which the SBR is SSBR B.

Composition 3: Formula F1 in which the SBR is SSBR C.

Composition 4: Formula F1 in which the SBR is SSBR A and which additionally contains 0.8 pce of free dodecylhexamethyleneimine (DDCHMI).

Composition 1 is a control composition, while Compositions 2, 3 and 4 are in conformity with the invention.

5 To prepare the mixtures which lead to the compositions, a two-stage thermomechanical operation is carried out which lasts 5 and 4 minutes, respectively, using an internal paddle mixer at an average paddle speed of 45 rpm, until attaining a maximum temperature of 160°C. The finishing stage is performed at 30°C. In the case of Composition 4, the addition of the free amine (DDCHMI) is performed with the aid of the internal mixer during the first stage of the thermomechanical operation.

All compositions are vulcanized at 150°C for 50 minutes.

The resulting properties of Compositions 1 to 4 in both the non-vulcanized state and the vulcanized state are compared with each other.

The results are listed in Table 1.

**Table 1**

	1	2	3	4
Compositions	F1	F1	F1	F1+0.8pce amine
	SSBRA	SSBR B	SSBR C	SSBR A
Initiator	nBuli	HMINli	nBuli	NBuli
Stopper	MeOH	MeOH	MeOH+Amine	MeOH
	control	invention	invention	invention

5 Properties in the nonvulcanized state:

ML(1+4) 100°	51	55	54	51
--------------	----	----	----	----

Properties in the vulcanized state:

Shore	64.0	58.8	56.5	59.4
EM10	5.10	3.83	3.48	3.95
EM 100	1.72	1.71	1.61	1.57
EM 300	2.03	2.26	2.19	1.96
EM300/EM100	1.18	1.32	1.36	1.25
Scott20° Fr	18.1	20.9	20.4	19.0
Er%	520	580	580	570
HL	33.2	25.1	26.1	29.4

(def. = 40%)

Dynamic properties under deformation (10Hz/def -.15% - 50%):

DeltaG*	4.05	1.09	1.03	1.95
tgδ	0.355	0.216	0.224	0.266
G"	1.230	0.433	0.436	0.690

Table 1 shows that the three compositions according to the invention, Compositions 2 to 4, have hysteretic properties that are considerably improved in comparison to the control composition 1, this being so both at low deformation ( $tg\delta$  values and  $G''$ ) and at high deformation (HL values), and that these compositions of the invention have reinforcing properties and rupture qualities that are considerably better than those of the control composition (EM300/EM100 and Scott20° values). Thus, this improvement can be obtained with a non-functionalized polymer (Compositions 3 and 4).

It is further noted that Composition 4, while being better than the control composition for the above reasons, has properties that are slightly poorer than those of Compositions 2 and 3, which shows that the introduction of the amine bonded to the polymer or perfectly dispersed in the elastomeric matrix by adding it in solution form before stripping is more effective for improving the hysteretic properties and mechanical cohesion.

#### Example 2

The same basic formula F1 as in Example 1, and the following three SSBR's are used.

- SSBR D:  $T_g = -38^\circ\text{C}$ ; 1,2 content = 41%; styrene content = 26%;  $ML(1+4)_{100^\circ} = 70$
- SSBR E:  $T_g = -38^\circ\text{C}$ ; 1,2 content = 41%; styrene content = 26%; functionalized with hexamethylcyclotrisiloxane (D3);  $ML(1+4)_{100^\circ} = 60$
- SSBR F:  $T_g = -38^\circ\text{C}$ ; 1,2 content = 41%; styrene content = 26%; starred by means of

tin tetrachloride;  $ML(1+4)100^\circ = 70$

- SSBR G:  $T_g = -38^\circ\text{C}$ ; 1,2 content = 41%; styrene content = 26%; functionalized with bis-diethylaminobenzophenone;  $ML(1+4)100^\circ = 70$

All these elastomers are synthesized by a continuous process, in the following manner:

## 5 Preparation of SSBR's D, E and G

10 Into a reactor of 14 L useful capacity and equipped with a turbine-type stirrer are continuously introduced cyclohexane, butadiene, styrene and tetrahydrofuran in mass proportions of 100 : 10.00 : 4.30 : 0.3, respectively, as well as a solution of n-butyllithium (SSBR D and G: 460 micromoles of active n-BuLi per 100 grams of monomers; SSBR E: 500 micromoles). The flow rates of these different solutions are calculated so that the dwelling time is 40 minutes under strong agitation. The temperature is kept constant at  $60^\circ\text{C}$ . At the exit from the reactor, the conversions measured on samples are 85% (SSBR D and G) and 88% (SSBR E). The three SBR's contain 26% incorporated styrene (by weight) and have a 1,2 bond content of 41% for the butadiene part.

15 SSBR D is stopped by the addition of methanol (MeOH/n-BuLi ratio = 1.5).

SSBR E is stopped by the addition of D3 (D3/n-BuLi ratio = 0.40).

SSBR G is stopped by the addition of bis-diethylaminobenzophenone (BDEAB/n-BuLi ratio = 1.5).

For the two polymers E and G, a contact time of 40 minutes between polymer and amine is assured by means of a second reactor stirred and heated at 60°C.

For the three elastomers, there is added 0.8 pce of 2,2'-methylene bis(4-methyl-6-tert.-butylphenol) and 0.2 pce of N-(1,3-dimethylbutyl)-N-phenyl-p-phenylenediamine used as antioxidants. The polymers are separated from the solvent by stripping the solvent by steam distillation, then dried on a 100°C tool for 10 minutes. The inherent viscosities (in toluene) are measured before the stripping operation.

The function content  $[\text{Si}(\text{CH}_3)_2\text{OH}]$  is determined by proton NMR assay.

The  $^1\text{H}$  NMR assay is carried out on a sample which has undergone three dissolution cycles in toluene, and coagulation in methanol, to eliminate any possible trace of residual hexamethylcyclotrisiloxane (not linked to the polymer). The molecular mass of SSBR E is 175,000 g mole<sup>-1</sup>.

The  $^1\text{H}$  NMR spectrum of dimethyl-silanol-functionalized SSBR E is characterized by peaks at 0.05 ppm and 0.1 ppm corresponding to the  $\text{Si}(\text{CH}_3)_2$  group. The content of  $[\text{Si}(\text{CH}_3)_2\text{OH}]$  units is 4.6 mEq./kg, or 81% of functionalized chains.

The amount of  $[(\text{C}_2\text{H}_5)_2\text{N}-\text{C}_6\text{H}_4]_2\text{COH}$  units of SSBR G is 5 mEq./kg, or 90% of functionalized chains. The molecular mass of SSBR G is 180,000 g mole<sup>-1</sup>.

### Preparation of SSBR F

SSBR F is synthesized under conditions analogous to those described for SSBR D and E, except for the amount of BuLi used and the mode of stoppage.

The amount of active n-BuLi is 900 micromoles per 100 grams of monomers.

At the exit from the reactor, the conversion is 92% (viscosity: 1.26 dL/g), the tin tetrachloride is injected upstream of a static mixer comprising 24 elements. The antioxidants are added 5 minutes after injection of SnCl<sub>4</sub>. The viscosity after starring is 1.85 dL/g.

Eight compositions numbered 5 to 11 are prepared in the following manner:

Composition 5: Formula F1 in which the SBR is SSBR D;

Composition 6: Composition 5 to which 0.8 pce of DDCHMI has been added;

Composition 7: Formula F1 in which the SBR is SSBR E;

Composition 8: Composition 7 to which 0.8 pce of DDCHMI has been added;

Composition 9: Formula F1 in which the SBR is SSBR F;

Composition 10: Composition 9 to which 0.8 pce of DDCHMI has been added;

Composition 11: Formula F1 in which the SBR is SSBR G;

Composition 12: Composition 11 to which 0.8 pce of DDCHMI has been added.

The preparation of the compositions by mixing, and their vulcanization, are carried out as in Example 1. For Compositions 6, 8, 10 and 12, the amine was added using an internal mixer during the first stage of the thermo-mechanical operation.

Compositions 5, 7, 9, 11 and 12 are control compositions, while Compositions 6, 8 and 10 are in conformity with the invention.

The tests are performed under the same conditions as in Example 1, and the results are listed in Table 2.

006740" 236236.1



**Table 2**

Compositions	5	6	7	8	9	10	11	12
	F1	F1+DDCHMI 0.8pce	F 1	F1+DDCHMI 0.8pce	F1	F1+DDCHMI 0.8pce	F1	F1+DDCHMI 0.8pce
		SSBR D		SSBR E		SSBR F		SSBR G
Stopper		MeOH		D3		SnCl <sub>4</sub>		BDEAB

Properties in the nonvulcanized state:

ML(1+4) 100°	79	76	87	86	43	42	85	80
-----------------	----	----	----	----	----	----	----	----

Properties in the vulcanized state:

Shore	63.3	59.0	59.2	58.8	60.8	58.7	62.8	59.7
EM10	5.12	4.05	3.89	3.72	4.53	4.13	5.00	4.10
EM100	1.57	1.43	1.61	1.69	1.54	1.46	1.58	1.48
EM300	1.75	1.73	2.01	2.23	1.74	1.71	1.81	1.81
EM300/EM1	1.11	1.21	1.25	1.32	1.13	1.17	1.14	1.22
Scott20° Fr	21.1	20.9	24.0	25.0	17.6	18.1	21.6	21.8
Er%	650	680	610	590	600	620	610	640
HL	33.1	29.1	24.6	22.5	37.4	35.6	32.4	28.6

(def = 40%)

Dynamic properties under deformation (10Hz/def 0.15% - 50%):

DeltaG*	4.81	2.70	1.48	1.18	3.00	2.23	3.43	2.12
tgδ	0.370	0.281	0.249	0.228	0.336	0.305	0.321	0.265
G"	1.430	0.890	0.576	0.488	1.060	0.843	1.150	0.840

Compositions 6, 8 and 10 according to the invention show that, with any functionalized or starred elastomer, the addition of free amine provides significant improvement in hysteresis and reinforcement, compared with the properties obtained with the conventional compositions prepared without the addition of free amine, and even in comparison to those which comprise a polymer having aromatic dialkylamine functions at the chain end.

### Example 3

The following basic formulas F2 and F3 are used.

Formula F2:

SBR	100
Silica (1)	60
Aromatic oil	20
Linking agent (2)	4.8
ZnO	2.5
Stearic acid	1.5
Antioxidant (6PPD)	1.9
Ozone wax C32T	1.5
Sulfur	1.1
Sulfenamide (CBS)	2

Diphenylguanidine 1.1

(1) = ZEOSIL 1165 silica (manufactured by Rhône-Poulenc)

(2) = Linking agent: Si69 (Degussa)

Formula F3:

5	SBR	100
	Silica (1)	40
	N 234 Black	40
	Aromatic oil	40
	Linking agent (2)	3.2
10	ZnO	2.5
	Stearic acid	1.5
	Antioxidant (6PPD)	1.9
	Ozone wax C32T	1.5
	Sulfur	1.1
15	Sulfenamide (CBS)	2
	Diphenylguanidine	0.8

(1) = ZEOSIL 1165 silica (manufactured by Rhône-Poulenc)

(2) = Linking agent: Si69 (Degussa).

With the aid of these two basic formulations, compositions were prepared using the

elastomers SSBR A and SSBR B of Example 1.

These compositions are as follows:

Composition 11: Formula F2, with SSBR A as the SBR;

Composition 12: Formula F2, with SSBR B as the SBR;

Composition 13: Formula F2, with SSBR A as the SBR, and additionally containing 0.8  
pce of DDCHMI;

Composition 14: Formula F3, with SSBR A as the SBR;

Composition 15: Formula F3, with SSBR B as the SBR.

Compositions 11 and 14 are control compositions, while Compositions 12, 13 and 15 are  
in conformity with the invention.

The preparation of the compositions by mixing and their vulcanization are carried out as  
in Example 1. The addition of the free amine to Composition 13 is done with the aid of the  
internal mixer during the first stage of this thermo-mechanical operation.

The results are listed in Tables 3 and 4.

**Table 3**

Compositions	11	12	13
Formula	F2	F2	F2+DDCHMI
			0.8pce
SSBR	SSBR A	SSBR B	SSBR A
Initiator	NBuli	HMINLi	nBuli
Stopper	MeOH	MeOH	MeOH

Properties in the nonvulcanized state:

ML(1+4) 100°	64	78	69
--------------	----	----	----

Properties in the nonvulcanized state:

Shore	64.2	57.2	55.3
EM10	5.41	3.68	3.38
EM 100	1.88	1.72	1.52
EM 300	2.20	2.44	2.13
EM300/EM100	1.17	1.42	1.40
Scott20° Fr	22.8	23.5	23.1
Er%	570	540	570
HL	27.2	18.9	22.8

(def = 35%)

Dynamic properties under deformation (10Hz/def 0.15% - 50%):

DeltaG*	3.07	0.39	0.38
tgδ	0.281	0.143	0.148
G"	0.878	0.247	0.252

5

**Table 4**

Compositions	14	15
Formula	F3	F3
SSBR	SSBR A	SSBR B
Initiator	nBuli	HMINLi
Stopper	MeOH	MeOH

Properties in the nonvulcanized state:

ML(1+4) 100°	56	72
--------------	----	----

Properties in the vulcanized state:

Shore	63.4	61.9
EM10	5.22	4.77
EM 100	1.62	1.75
EM 300	1.72	2.07
EM300/EM100	1.06	1.18
Scott20° Fr	17.8	19.0
Er%	650	580
HL	42.1	35.3

(def = 40%)

Dynamic properties under deformation (10Hz/def 0.15% - 50%):

DeltaG*	6.04	3.91
tgδ	0.421	0.365
G"	1.770	1.250

This table shows that, in the case of a filler based on carbon black and silica in a 50 : 50 mass proportion, the addition of amine to the elastomer chain improves the properties of hysteresis and reinforcement in comparison to the properties obtained with the corresponding control mixture 14, whose elastomer does not contain amine.

#### Example 4

In this example, the following four compositions are used.

Composition 16: Basic formula F1 in which the SBR is SSBR A;

Composition 17: Composition 16 wherein the DPG is replaced with 1.9 pce of dodecylhexamethyleneimine (DDCHMI), or 7.1 mmols, the DDCHMI content in mmols being the same as that of DPG in basic formula F1 (also 7.1 mmols);

Composition 18: Composition 16 in which the DPG content is 2.5 pce (or 11.8 mmols) instead of 1.50 pce (7.1 mmols);

Composition 19: Composition 16, to which 1.2 pce (4.5 mmols) of DDCHMI has been added.



Composition 19 is the only one that is in conformity with the invention; Compositions 16 to 18 are control compositions.

The compositions are prepared and vulcanized as in Example 1. The addition of amines in Compositions 17 and 19 is carried out with the aid of the internal mixer during the first stage of this thermomechanical operation.

The results are listed in Table 5.

**Table 5**

Compositions	16	17	18	19
Formula	F1	F1	F1	F1
DPG (pce) (mmol)	1.50 (7.1)	0	2.5 (11.8)	1.5 (7.1)
DDCHMI (pce) (mmol)	0	1.9 (7.1)	0	1.2 (4.5)

Properties in the nonvulcanized state:

ML(1+4)100°	51	46	47	54
-------------	----	----	----	----

Properties in the vulcanized state:

Shore	64.0	63.3	62.8	60.0
EM10	5.10	5.17	4.32	4.15
EM 100	1.72	1.50	1.89	1.65
EM 300	2.03	1.57	2.59	2.07
EM300/EM100	1.18	1.05	1.37	1.25
Scott20° Fr	18.1	18.3	20.4	20.8
Er%	520	670	500	560
HL	33.2	38.4	26.2	29.3

(def. = 35%)

Dynamic properties under deformation (10Hz/def 0.15%-50%)

DeltaG*	4.05	3.43	2.71	1.64
tgδ	0.355	0.308	0.306	0.254
G"	1.230	1.050	0.872	0.605

This example shows that the most effective composition for reducing the hysteresis at low deformations is the composition in which both DPG and DFDCHMI are present (Composition 19).

Example 5

The following four compositions are used:

Composition 20: Basic formula F1 where the SBR is SSBR A;

Composition 21: Composition 20 to which 0.4 pce (2.2 mmoles) of dicyclohexylamine (DCHA) has been added;

Composition 22: Composition 20 to which 0.8 mmoles (3.8 mmoles) of DCHA has been added;

Composition 23: Composition 20 to which 0.8 pce (3 mmoles) of DDCHMI has been added.

Composition 20 is the control composition, while Compositions 21 to 23 are in conformity with the invention.

The compositions are prepared and vulcanized as in Example 1. The addition of the amines for Compositions 21, 22 and 23 is done with the aid of the internal mixer during the first stage of this thermomechanical operation.

The results are given in Table 6.

006740 282940

**Table 6**

Compositions	20	21	22	23
Formula	F1	F1	F1	F1
DCHA (pce/mmoles)	0	0.4/2.2	0.8/3.8	
DDCHMI (pce/mmmoles)	0	0	0	0.8/3

Properties in the nonvulcanized state:

ML(1+4)100°	51	51	50	51
-------------	----	----	----	----

Shore	64.0	63.1	61.8	59.4
EM10	5.10	4.78	4.79	3.95
EM 100	1.72	1.70	1.72	1.57
EM 300	2.03	2.03	2.06	1.96
EM300/EM100	1.18	1.19	1.20	1.25
Scott20° Fr	18.1	19.8	20.3	19.0
Er%	520	550	560	570
HL	33.6	30.5	30.3	29.4
(def. = 35%)				

Dynamic properties under deformation (10 Hz/def 0.15% - 50%)

DeltaG*	4.05	3.42	3.23	1.95
tgδ	0.355	0.327	0.322	0.266
G"	1.230	1.070	1.010	0.690

This example shows that addition of amines DCHA and DDCHMI makes it possible to reduce the hysteresis at low and high deformations in comparison to the control. However, DDCHMI (Composition 23) is more effective.

Example 6

The following compositions are used:

Composition 24: Formula F1 where the SBR is SSBR A;

Composition 25: Composition 24 to which 0.8 pec of DDCHMI has been added;

Composition 26: Composition 24 where 5.7 pce of Si266 made by Degussa (bispropyltriethoxysilane disulfide) was used instead of 6.4 pce of Si69;

Composition 27: Composition 26, which additionally contains 0.8 pce of DDCHMI.

Compositions 25 and 27 are according to the invention; compositions 24 and 26 are control compositions.

The compositions are prepared and vulcanized as in Example 1. For Compositions 25 and 27, the amines are added with the aid of the internal mixer during the first stage of this thermomechanical operation. The results are listed in Table 7.

Table 7

Compositions	24	25	26	27
Formula	F1	F1	F1	F1
Si69 (pce)	6.4	6.4	0	0
Si266 (pce)	0	0	5.7	5.7
DDCHMI (pce)	0	0.8	0	0.8
Properties in the nonvulcanized state:				
ML(1+4)100°	51	51	49	48
Properties in the nonvulcanized state:				
Shore	64.0	59.4	59.0	58.2
EM10	5.10	3.95	4.09	4.01
EM 100	1.72	1.57	1.20	1.18
EM 300	2.03	1.96	1.19	1.11
EM300/EM100	1.18	1.25	0.99	0.94
Scott20° Fr	18.1	19.0	16.1	15.0
Er%	520	570	720	750
HL	33.2	29.4	42.8	44.1
(def = 35%)				
Dynamic properties under deformation (10Hz/def 0.15% - 50%):				
DeltaG*	4.05	1.95	2.68	2.38
tgδ	0.355	0.266	0.312	0.295
G"	1.230	0.690	0.905	0.818

This example shows that the addition of DDCHMI permits a major improvement of hysteresis at low deformations in the case of a linking agent that is in conformity with the invention (Si69 or Si266), and that the use of Si69 (comprising four sulfur atoms in the molecule) gives better results with regard to hysteresis at low and high deformations and with regard to reinforcement than does the use of Si266 which only has two sulfur atoms in its molecule.

#### Example 7

The following compositions are used:

Composition 28: Formula F1 in which the SBR is SSBR A;

Composition 29: Formula F1 in which the SBR is SSBR B;

Composition 30: Composition 29 which only contains 3.2 pce of Si69;

Composition 31: Composition 29 devoid of linking agent;

Composition 32: Formula F1 in which the SBR is SSBR C;

Composition 33: Composition 32, in which the Si69 content is only 3.2 pce;

Composition 34: Composition 32 devoid of linking agent.

Compositions 29, 30, 32 and 33 are in accordance with the invention; Compositions 28, 31 and 34 are control compositions.

The compositions are prepared and vulcanized as in Example 1.

The results are given in Table 8.



**Table 8**

Compositions	28	29	30	31	32	33	34
Formula	F1	F1	F1	F1	F1	F1	F1
Si69 (pce)	6.4	6.4	3.2	0	6.4	3.2	0
SSBR	A	B	B	B	C	C	C
Properties in the non-vulcanized state:							
ML(1+4)100°	51	55	68	147	54	59	13
Properties in the vulcanized state:							
Shore	64.0	58.8	60.0	66.8	56.5	59.2	65.0
EM10	5.10	3.83	4.64	7.65	3.48	4.33	7.28
EM 100	1.72	1.71	1.36	0.94	1.61	1.37	0.78
EM 300	2.03	2.26	1.52	0.52	2.19	1.59	0.41
EM300/EM100	1.18	1.32	1.12	0.55	1.36	1.16	0.53
Scott20° Fr	18.1	20.9	18.0	8.0	20.4	18.6	7.1
Er%	520	580	720	1030	580	680	1020
HL	33.2	25.1	33.5	54.7	26.1	33.7	59.9
(def = 35%)							
Dynamic properties under deformation (10Hz/def 0.15% - 50%):							
DeltaG*	4.05	1.09	1.74	4.32	1.03	1.77	5.1
tgδ	0.355	0.216	0.242	0.263	0.224	0.252	0.2
G"	1.230	0.433	0.590	1.110	0.436	0.618	1.3

This example shows that the presence of amino groups is not sufficient to improve the balance between hysteretic properties and mechanical cohesion; also necessary is the presence of a linking agent according to Formula (I), and the content of linking agent or ensemble of linking agents in accordance with this formula should preferably be at least equal to 4% by weight of the content of the silica or mixture of silicas, which is the case in Compositions 29, 30, 32 and 33. The results are better for Compositions 29 and 32 where the linking agent content is more than 4 % of the weight of silica.

It is to be understood that the invention is not limited to the above-described embodiments, on the basis of which it is possible to envisage other modes of carrying out the invention.

09/462387

FILE NO. A32851-PCT-USA-070338.0556

428 Rec'd PCT/PTO 06 JAN 2000  
PATENT**ABSTRACT**

The invention concerns a rubber composition vulcanizable in sulphur characterized in that it comprises: a) at least one polymer selected from the group consisting of diene polymers, olefin/diene monomer copolymers and halogenated iso-olefin/para-alkylstyrene copolymers; b) silica as filler; c) at least a sulphured silane enabling the bond between the silica and the polymer; d) at least a substituted guanidine; and in that it has at least one of the following characteristics: it comprises at a diene polymer containing at least a terminal amino group of an aliphatic or cycloaliphatic amine which is itself bound at the chain end, the polymer being thus devoid of alkoxysilane group and silanol group; the composition comprises at least a free aliphatic or cycloaliphatic amine. The invention also concerns a tire and tire tread comprising such a composition.

006740-482940

**Declaration and Power of Attorney for Patent Application****Déclaration et Pouvoirs pour Demande de Brevet****French Language Declaration**

En tant que l'inventeur nommé ci-après, je déclare par le présent acte que:

Mon domicile, mon adresse postale et ma nationalité sont ceux figurant ci-dessous à côté de mon nom.

Je crois être le premier inventeur original et unique (si un seul nom est mentionné ci-dessous), ou l'un des premiers co-inventeurs originaux (si plusieurs noms sont mentionnés ci-dessous) de l'objet revendiqué, pour lequel une demande de brevet a été déposée concernant l'invention intitulée

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

**SILICA-CONTAINING RUBBER  
COMPOSITION VULCANIZABLE WITH  
SULFUR**

Cette déclaration est du type suivant:

- |                                 |                                     |
|---------------------------------|-------------------------------------|
| original                        | <input type="checkbox"/>            |
| modèle                          | <input type="checkbox"/>            |
| phase nationale du PCT          | <input checked="" type="checkbox"/> |
| divisionnaire                   | <input type="checkbox"/>            |
| continuation                    | <input type="checkbox"/>            |
| continuation en parties (C-E-P) | <input type="checkbox"/>            |

This declaration is of the following type:

- |                              |                                     |
|------------------------------|-------------------------------------|
| original                     | <input type="checkbox"/>            |
| design                       | <input type="checkbox"/>            |
| national stage of PCT.       | <input checked="" type="checkbox"/> |
| divisional                   | <input type="checkbox"/>            |
| continuation                 | <input type="checkbox"/>            |
| continuation-in-part (C-I-P) | <input type="checkbox"/>            |

et dont la description est fournie ci-joint à moins que la case suivante n'ait été cochée:

- ☐ a été déposée le \_\_\_\_\_  
sous le numéro de demande des Etats-Unis ou le numéro de  
demande international PCT \_\_\_\_\_  
et modifiée le \_\_\_\_\_  
(le cas échéant).

the specification of which is attached hereto unless the following box is checked:

- ☒ was filed on 1/6/00  
as United States Application Number or PCT  
International Application Number  
09/462,387 and was amended on \_\_\_\_\_  
(if applicable).

Je déclare par le présent acte avoir passé en revue et compris le contenu de la description ci-dessus, revendications comprises, telles que modifiées par toute modification dont il aura été fait référence ci-dessus.

Je reconnais devoir divulguer toute information pertinente à la brevetabilité, comme défini dans le Titre 37, § 1.56 du Code fédéral des réglementations.

- ☐ Conformément aux termes de cette obligation, les informations exigées sont jointes 37 CFR 1.98 aux présentes.

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56.

- ☐ In compliance with this duty there is attached an information disclosure statement. 37 CFR 1.98.

\* Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number

## French Language Declaration

Je revendique par le présent acte avoir la priorité étrangère, en vertu du Titre 35, § 119(a)-(d) ou § 365(b) du Code des Etats-Unis, sur toute demande étrangère de brevet ou certificat d'inventeur ou, en vertu du Titre 35, § 365(a) du même Code, sur toute demande internationale PCT désignant au moins un pays autre que les Etats-Unis et figurant ci-dessous et, en cochant la case, j'ai aussi indiqué ci-dessous toute demande étrangère de brevet, tout certificat d'inventeur ou toute demande internationale PCT ayant une date de dépôt précédant celle de la demande à propos de laquelle une priorité est revendiquée.

Prior foreign application(s)

Demande(s) de brevet antérieure(s)

97/08839	France
(Number)	(Country)
(Numéro)	(Pays)

(Number)	(Country)
(Numéro)	(Pays)

(Number)	(Country)
(Numéro)	(Pays)

Je revendique par le présent acte tout bénéfice, en vertu du Titre 35, § 119(e) du Code des Etats-Unis, de toute demande de brevet provisoire effectuée aux Etats-Unis et figurant ci-dessous.

(Application No.)  
(N° de demande)

(Application No.)  
(N° de demande)

Je revendique par le présent acte tout bénéfice, en vertu du Titre 35, § 120 du Code des Etats-Unis, de toute demande de brevet effectuée aux Etats-Unis, ou en vertu du Titre 35, § 365(c) du même Code, de toute demande internationale PCT désignant les Etats-Unis et figurant ci-dessous et, dans la mesure où l'objet de chacune des revendications de cette demande de brevet n'est pas divulgué dans la demande antérieure américaine ou internationale PCT, en vertu des dispositions du premier paragraphe du Titre 35, § 112 du Code des Etats-Unis, je reconnais devoir divulguer toute information pertinente à la brevetabilité, comme défini dans le Titre 37, § 1.56 du Code fédéral des réglementations, dont j'ai pu disposer entre la date de dépôt de la demande antérieure et la date de dépôt de la demande nationale ou internationale PCT de la présente demande:

PCT/EP98/03917	June 26, 1998
(Application No.)	(Filing Date)
(N° de demande)	(Date de dépôt)

(Application No.)	(Filing Date)
(N° de demande)	(Date de dépôt)

Je déclare par le présent acte que toute déclaration ci-incluse est, à ma connaissance, véridique et que toute déclaration formulée à partir de renseignements ou de suppositions est tenue pour véridique; et de plus, que toutes ces déclarations ont été formulées en sachant que toute fausse déclaration volontaire ou son équivalent est passible d'une amende ou d'une incarcération, ou des deux, en vertu de la Section 1001 du Titre 18 du Code des Etats-Unis, et que de telles déclarations volontairement fausses risquent de compromettre la validité de la demande de brevet ou du brevet délivré à partir de celle-ci.

I hereby claim foreign priority under Title 35, United States Code, § 119(a)-(d) or § 365 (b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below, and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

Priority Claimed

Droit de priorité revendiqué

July 9, 1997	[X]
(Day/Month/Year Filed)	
(Jour/Mois/Année de dépôt)	

(Day/Month/Year Filed)	[ ]
(Jour/Mois/Année de dépôt)	

(Day/Month/Year Filed)	[ ]
(Jour/Mois/Année de dépôt)	

I hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below.

(Filing Date)  
(Date de dépôt)

(Filing Date)  
(Date de dépôt)

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

pending
(Status) (patented, pending, abandoned)
(Statut) (breveté, en cours d'examen, abandonné)

(Status) (patented, pending, abandoned)
(Statut) (breveté, en cours d'examen, abandonné)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number

### French Language Declaration

POUVOIRS: En tant que l'inventeur cité, je désigne par la présente l'(les) avocat(s) et/ou agent(s) suivant(s) pour qu'ils poursuive(nt) la procédure de cette demande de brevet et traite(nt) toute affaire s'y rapportant avec l'Office des brevets et des marques: (*mentionner le nom et le numéro d'enregistrement*).

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith: (*list name and registration number*)

21  
Dana M. Raymond, Reg. No. 18,540; Frederick C. Carver, Reg. No. 17,021; Francis J. Hone, Reg. No. 18,662; Joseph D. Garon, Reg. No. 20,420; Arthur S. Tenser, Reg. No. 18,839; Ronald B. Hildreth, Reg. No. 19,498; Thomas R. Nesbitt, Jr., Reg. No. 22,075; Robert Neuner, Reg. No. 24,316; Richard G. Berkley, Reg. No. 25,465; Richard S. Clark, Reg. No. 26,154; Bradley B. Geist, Reg. No. 27,551; James J. Maune, Reg. No. 26,946; John D. Murnane, Reg. No. 29,836; Henry Tang, Reg. No. 29,705; Robert C. Scheinfeld, Reg. No. 31,300; John A. Fogarty, Jr., Reg. No. 22,348; Louis S. Sorell, Reg. No. 32,439; Rochelle K. Seide, Reg. No. 32,300; Gary M. Butter, Reg. No. 33,841; Marta E. Delsignore, Reg. No. 32,689; and Lisa B. Kole, Reg. No. 35,225

Send Correspondence to:

Adresser toute correspondance à:

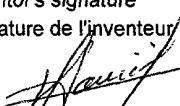
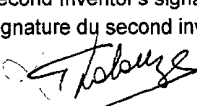
BAKER BOTTS L.L.P.  
30 Rockefeller Plaza  
New York, New York 10112  
Customer Number: 21003

Direct Telephone Calls to:

Adresser tout appel téléphonique à:

(*nom et numéro de téléphone*)

Baker Botts L.L.P.  
212-408-2500

Full name of sole or first inventor Nom complet de l'unique ou premier inventeur <u>MARC DANIEL</u>	Full name of second joint inventor, if any Nom complet de second co-inventeur, le case échéant <u>Gérard Labauze</u>
Inventor's signature Signature de l'inventeur 	Second Inventor's signature Signature du second inventeur 
Date <u>April 15, 2000</u>	Date <u>April 3, 2000</u>
Residence Domicile <u>Greer, South Carolina SC</u>	Residence Domicile <u>Clermont-Ferrand/France FRX</u>
Citizenship Nationalité France	Citizenship Nationalité France
Post Office Address Adresse postale 125 River Way Drive Greer, South Carolina	Post Office Address Adresse postale 3, rue du Parc de Montjuzet F-63100 Clermont Ferrand France

(Fournir les mêmes renseignements et la signature de tout co-inventeur supplémentaire.)

(Supply similar information and signature for third and subsequent joint inventors.)